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# **MATHEMATICS**



**THE INVESTIGATIONS OF THE FORCED OSCILLATIONS SET UP  
IN AN AEROPLANE BY PERIODIC GUSTS OF WIND,  
WITH SPECIAL REFERENCE TO THE CASE OF  
SYNCHRONY WITH THE FREE OSCILLATIONS.**

By

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The "Phugoid theory" propounded by Lanchester and elaborated by Bryan furnishes us with the path and the periods of the natural oscillations of an aeroplane which has been plunged with a velocity slightly different from its natural velocity. The equation of the path given by Lanchester for an aerodone is

$$\cos \theta = \frac{H}{3H_n} + \frac{C}{\sqrt{H}}$$

when  $\theta$  is the angle of path to horizon,  $H_n$  the natural height i.e., the height of fall corresponding to the actual velocity and  $C$  a variable parameter. For different value of  $C$  Lanchester has plotted the flight-path in his "Aerial Flight" and discussed their various possibilities. From the form of the equation it is evident that the path is a periodic one and Bryan in his Stability in Aviation proceeding in a more mathematical and extended way finds that the periods of the natural oscillations are given by the roots of a bi-quadratic which he has solved for particular cases. In general he finds that the motion consists of 2 distinct periodic oscillations, the time period of one is very long and another comparatively short. In fact Thompson solving a particular case of an aeroplane with the natural velocity 100 ft. per sec. finds that the roots of Bryan's bi-quadratic are given by

$$\lambda^4 + 5.2\lambda^3 + 11.6\lambda^2 + 1.38\lambda + 1.04 = 0$$

so that the roots are

$$\lambda = -2.64 \pm 2.14\sqrt{-1}$$

$$\lambda = -.089 \pm .297\sqrt{-1}$$

It is worth noticing that the first pair of roots are about seven times the second pair, while the damping factor in the former case is about 70 times that of the second. So that the longer oscillations are damped out the quicker, a lucky fact indeed for aeronautic.

The study of these free oscillations of an aeroplane by Lanchester, Bryan and a host of others has given sufficient data for aeronautic engineers to build stable aeroplane but one point of danger still remains which has been the doom of many an aviator. It is well known that if a periodic disturbance acts on a system which has its own natural period of oscillation and if the periods of the disturbance be almost equal or equal to the natural period, the system may be thrown in a violent state of oscillation which may prove dangerous. It is one redeeming feature in the motion of an aeroplane that its oscillations are damped which may sometimes check the abovementioned pernicious tendency. In order to study this problem mathematically I have undertaken the following work. It has been found that under certain qualifying conditions the aeroplane may have a stable motion in the face of such a periodic gust of wind. The problem could not be very thoroughly treated as experimental datas and theoretical knowledge of air forces is still meagre in spite of the enormous strides the science has taken during and since the war in the hands of Prandtl, Kiffel and Bairstow.

We start by writing down the general equations of motions of Rigid Dynamics. Taking the centre of mass of the aeroplane as the origin of co-ordinates and 3 rectangular axes fixed relatively to the aeroplane and moving with it in space and using the following notations

$W,$	weight of the aeroplane.
$A, B, C,$	moments of inertia about the axes.
$D, E, F,$	corresponding products of inertia.
$u, v, w$	components of translational velocity.
$p, q, r$	„ of angular velocity.
$h_1, h_2, h_3$	„ of angular momentum.

we have the following equations of motion :

$$W \left( \frac{du}{gdt} + \frac{qv}{g} - \frac{rw}{g} \right) = \text{Acc. force along the } x\text{-axis}$$

and two similar equations, also

$$\frac{dh_1}{gdt} + \frac{qh_2}{g} - \frac{rh_3}{g} = \text{Acc. torque about the } x\text{-axis}$$

and two similar equations, and

$$h_1 = Ap - Fq - Er$$

$$h_2 = Bq - Dr - Fp$$

$$h_3 = Cr - Ep - Dq$$

In the first place, let the aeroplane be flying steadily in a horizontal straight line. Let this be the axis of  $x$  (the line parallel to the line of flight and passing through the C. G.) and a line drawn vertically downwards through the C-G, the  $y$ -axis and a horizontal line perpendicular to these the axis of  $z$ .

If the aeroplane be turned in any other directions the following angular co-ordinates will specify them :

Starting from an initial position, let us rotate the aeroplane about the  $y$ -axis through an angle  $\psi$  and then about the new position of the axis of  $z$  through an angle  $\theta$  and lastly about the final position of the  $x$ -axis through an angle  $\phi$ . The cosines of the angles between the old axis  $x_0y_0z_0$  and the new  $x_1y_1z_1$  are given by

$x_1$	$y_1$
$x_0 \quad \cos \theta \cos \psi,$	$\sin \phi \sin \psi - \cos \phi \cos \psi \sin \theta,$
$y_0 \quad \sin \theta,$	$\cos \theta \cos \phi,$
$z_0 \quad -\cos \theta \sin \psi,$	$\sin \phi \cos \psi + \cos \phi \sin \psi \sin \theta,$
$z_1$	
$\cos \phi \sin \psi + \sin \phi \cos \psi \sin \theta.$	
$-\cos \theta \sin \phi.$	
$\cos \phi \cos \psi - \sin \phi \sin \psi \sin \theta.$	

and the angular velocities  $p, q, r$  are given in terms of  $\theta, \phi, \psi$

$$p = \dot{\phi} + \dot{\psi} \sin \theta$$

$$q = \dot{\theta} \sin \phi + \dot{\psi} \cos \theta \cos \phi$$

$$r = \dot{\theta} \cos \phi - \dot{\psi} \cos \theta \sin \phi$$

The imposed forces and couples are due to (i) gravity (ii) the propeller thrust (iii) air resistances (iv) the periodic disturbances due to the gusts of wind.

The components of gravity along the axes are  $W \sin \theta$ ,  $W \cos \theta \cos \phi$ ,  $-W \cos \theta \sin \phi$  and the corresponding moments all vanishing.

The propeller thrust is assumed to act along a line parallel to the  $x$ -axis and at a point on the  $y$ -axis distant ' $h$ ' from the origin, then the components of thrusts are

Point of application,	O, $h$ , O
Force,	H, O, O
Torque,	O, O, $-Hh$

For the components of air resistances we assume that they reduce to  $X Y Z$  and  $L M N$  and these are taken positive when they tend to retard the corresponding motions of translation and rotations. The components of periodic gusts are  $P e^{mt}$ ,  $Q e^{mt}$ ,  $R' e^{mt}$ ,  $P' e^{mt}$ ,  $Q' e^{mt}$ ,  $R e^{mt}$  where ' $m$ ' is an imaginary quantity. Hence the equations of motion are in the case of symmetrical aeroplane (in which  $D=E=0$ )

$$\frac{W}{g} \left( \frac{du}{dt} + qw - rv \right) = W \sin \theta + H - X - P e^{mt}$$

$$\frac{W}{g} \left( \frac{dv}{dt} + ru - pw \right) = W \cos \theta \cos \phi - Y - Q e^{mt}$$

$$\frac{W}{g} \left( \frac{dw}{dt} + pv - qu \right) = -W \cos \theta \sin \phi - Z - R' e^{mt}$$

$$\frac{A}{g} \frac{dp}{dt} - \frac{F}{g} \frac{dq}{dt} + (C-B) \frac{rq}{g} + F \frac{pr}{g} = -L - P' e^{mt}$$

$$\frac{B}{g} \frac{dq}{dt} - \frac{F}{g} \frac{dp}{dt} + (A-C) \frac{pr}{g} - F \frac{qr}{g} = -M - Q' e^{mt}$$

$$\frac{C}{g} \frac{dr}{dt} + (B-A) \frac{pq}{g} - F \frac{p^2 - q^2}{g} = -Hh - N - R e^{mt}$$

Now suppose that the aeroplane was descending with uniform velocity  $U$  in the direction of the  $x$ -axis and let the axis make a constant angle  $\theta_0$  with the horizon, before the periodic gust began to operate; then initially  $u=U$ ,  $v, w, p, q, r$  zero, and the components of

the gusts absent and let the components of air resistances in this case be denoted by  $X_0, Y_0, Z_0, L_0, M_0, N_0$ . The equations of steady motion are

$$0 = W \sin \theta_0 + H - X_0$$

$$0 = W \cos \theta_0 - Y_0$$

$$0 = -Z_0$$

$$0 = -L_0$$

$$0 = -M_0$$

$$0 = -Hh - N_0$$

If now the periodic gust begins to operate we assume that the velocity components become  $U + u, v, w, p, q, r$  when  $u, v, w, p, q, r$  are all small. In the theory of small oscillations of dynamics we suppose that the squares and products of these velocities are negligible. The resistances  $X, Y, Z, L, M, N$  are functions of the velocity components  $U + u, v, w, p, q, r$  and the further assumption in dealing with small oscillations is that to a first approximation these resistances are expressible in the form

$$X = X_0 + uX_u + vX_v + wX_w + pX_p + qX_q + rX_r, \quad (\text{Bryan})$$

This assumption is common in treatise on theoretical mechanics as a first approximation when small oscillations are concerned. In our case since we have assumed the aeroplane as symmetrical

$$X = X_0 + uX_u + vX_v + rX_r,$$

$X_w, X_p, X_q$  being zero from considerations of symmetry. In small oscillations moreover  $\theta$  will differ from  $\theta_0$  by a small quantity  $\epsilon$  and  $\phi$  will be small, then

$$\sin \theta = \sin \theta_0 + \epsilon \cos \theta_0, \quad \cos \theta = \cos \theta_0 - \epsilon \sin \theta_0$$

$$\sin \phi = \phi \quad \cos \phi = 1$$

Hence the modified equations of motion become

$$\frac{W}{g} \frac{du}{dt} = W(\sin \theta_0 + \epsilon \cos \theta_0) + H - X_0 - uX_u - vX_v - rX_r - Pe^{mt}$$

$$\frac{W}{g} \left( \frac{dv}{dt} + rU \right) = W(\cos \theta_0 - \epsilon \sin \theta_0) - Y_0 - uY_u - vY_v - rY_r - Qe^{mt}$$

$$\frac{W}{g} \left( \frac{dw}{dt} - qU \right) = -W\phi \cos \theta_0 - Z_0 - wZ_w - pZ_p - qZ_q - R'e^{mt}$$



$$\frac{A}{g} \frac{dp}{dt} - \frac{F}{g} \frac{dq}{dt} = L_0 - wL_w - pL_p - qL_q - P'e^{m't}$$

$$\frac{B}{g} \frac{dq}{dt} - \frac{F}{g} \frac{dp}{dt} = M_0 - wM_w - pM_p - qM_q - Q'e^{m't}$$

$$\frac{C}{g} \frac{dv}{dt} = -Hh - N_0 - uN_u - vN_v - rN_r - Re^{m't}$$

We substitute from the equations of equilibrium and rearrange the equations in two groups, the first group containing those involving  $u, v, r$ , and the second group involving  $p, q, w$ . We thus get

$$\frac{W}{g} \frac{du}{dt} = W\epsilon \cos \theta_0 - uX_u - vX_v - rX_r - Pe^{m't}$$

$$\frac{W}{g} \left( \frac{dv}{dt} + rU \right) = -W\epsilon \sin \theta_0 - uY_u - vY_v - rY_r - Qe^{m't}$$

$$\frac{C}{g} \frac{dr}{dt} = -uN_u - vN_v - rN_r - Re^{m't}$$

and the second group

$$\frac{W}{g} \left( \frac{dw}{dt} - qU \right) = -W\phi \cos \theta_0 - wZ_w - pZ_p - qZ_q - R'e^{m't}$$

$$\frac{A}{g} \frac{dp}{dt} - \frac{F}{g} \frac{dq}{dt} = -wL_w - pL_p - qL_q - P'e^{m't}$$

$$\frac{B}{g} \frac{dq}{dt} - \frac{F}{g} \frac{dp}{dt} = -wM_w - pM_p - qM_q - Q'e^{m't}$$

The complementary functions of the first group of equations will give the longitudinal or symmetrical oscillations of the aeroplane and the second group give the lateral or transverse oscillations.

#### Group I.

To solve this group of equations we assume  $u, v$  and  $\epsilon$  each proportional to  $u_0 e^{m't}, v_0 e^{m't}, \epsilon_0 e^{m't}$  (as is the convention in the case of forced

oscillations) so that  $\frac{du}{dt} = mu_0 e^{m't}, \frac{dv}{dt} = mv_0 e^{m't}, \frac{d\epsilon}{dt} = m\epsilon_0 e^{m't}$  and since  $\theta = \theta_0$

$$+ \epsilon, \frac{d\epsilon}{dt} = \frac{d\theta}{dt} = m\epsilon = r,$$

Hence substituting these values in the first group and eliminating  $e^{mt}$  we get

$$\left( \frac{W}{g} m + X_u \right) u_0 + X_v \cdot v_0 + (mX_r - W \cos \theta) \epsilon_0 + P = 0$$

$$Y_u \cdot u_0 + \left( \frac{W}{g} m + Y_v \right) v_0 + \left\{ \left( \frac{W^U}{g} + Y_r \right) m + W \sin \theta \right\} \epsilon_0 + Q = 0$$

$$N_u \cdot u_0 + N_v \cdot v_0 + \left( \frac{C}{g} m^2 + N_r \cdot m \right) \epsilon_0 + R = 0$$

Solving these equations for  $u_0$ ,  $v_0$ ,  $\epsilon_0$  we get

$$= \begin{array}{c} u_0 \\ \left[ \begin{array}{cc} X_u, & mX_r - W \cos \theta, & P \\ \frac{W}{g} m + Y_u, & \left( \frac{W^U}{g} + Y_r \right) m + W \sin \theta, & Q \\ N_u, & \frac{C}{g} m^2 + N_r \cdot m, & R \end{array} \right] \\ \\ -v_0 \\ \left[ \begin{array}{cc} \frac{W}{g} m + X_u, & mX_r - W \cos \theta, & P \\ Y_u, & \left( \frac{W}{g} U + Y_r \right) m + W \sin \theta, & Q \\ N_u, & \frac{C}{g} m^2 + N_r \cdot m, & R \end{array} \right] \\ \\ \epsilon_0 \\ \left[ \begin{array}{cc} \frac{W}{g} m + X_u, & X_v, & P \\ Y_u, & \frac{W}{g} m + Y_v, & Q \\ N_u, & N_v, & R \end{array} \right] \end{array}$$

$$= \frac{-1}{F(m)} \begin{vmatrix} \frac{W}{g} m + X_u, X_v, & X_r \cdot m - W \cos \theta \\ Y_u, \frac{W}{g} m + Y_v, \left( W \frac{U}{g} + Y_r \right) m + W \sin \theta \\ N_u, & N_v, \frac{C}{g} m^2 + N_r \cdot m \end{vmatrix}$$

where  $F(m) = A_0 m^4 + B_0 m^3 + C_0 m^2 + D_0 m + E_0$  and these values of  $A_0$ ,  $B_0$ ,  $C_0$ ,  $D_0$  and  $E_0$  are given by Bryan

$$A_0 = CW^2$$

$$B_0/g = CW(X_u X_v + Y_u Y_v) + W^2 \cdot N_r$$

$$C_0/g^2 = C(X_u Y_v - X_v Y_u) + W[(Y_u N_v - Y_v N_u) + (X_u N_r - X_v N_u)] - \frac{W^2}{g} U \cdot N_v$$

$$D_0/g^3 = X_u(Y_v N_r - Y_r N_v) + X_v(Y_r N_u - Y_u N_r) + (Y_u N_v - Y_v N_u)X_r + W \frac{U}{g} (X_u N_v - X_v N_u) + \frac{W^2}{g} (N_u \cos \theta - N_v \sin \theta)$$

$$E_0/g^4 = \frac{W}{g} [-\cos \theta (Y_u N_v - Y_v N_u) - \sin \theta (X_u N_v - X_v N_u)]$$

Hence

$$u_0 = \frac{\begin{vmatrix} X_u, & mX_v - W \cos \theta & P \\ \frac{W}{g} + Y_u, \left( W \frac{U}{g} + Y_r \right) m + W \sin \theta, & Q \\ N_u, \frac{C}{g} m^2 + N_r \cdot m, & R \end{vmatrix}}{A_0 m^4 + B_0 m^3 + C_0 m^2 + D_0 m + E_0} = \frac{\phi(m)}{F(m)}$$

similarly  $v_0 = \frac{\psi(m)}{F(m)}$  and  $\epsilon_0 = \frac{\chi(m)}{F(m)}$ ; thus the complete values are

$$\begin{aligned} u &= a_1 e^{m_1 t} + a_2 e^{m_2 t} + a_3 e^{m_3 t} + a_4 e^{m_4 t} + u_0 e^{m t} \\ v &= b_1 e^{m_1 t} + b_2 e^{m_2 t} + b_3 e^{m_3 t} + b_4 e^{m_4 t} + v_0 e^{m t} \\ \epsilon &= c_1 e^{m_1 t} + c_2 e^{m_2 t} + c_3 e^{m_3 t} + c_4 e^{m_4 t} + \epsilon_0 e^{m t} \end{aligned}$$

where  $m_1, m_2, m_3, m_4$  are the roots of  $F(m)=0$

The motion of the aeroplane is almost exactly the same in the above case as it was when the gust did not act, only a periodic oscillation has been superadded on the other oscillations of the system, Hence its conditions of stability in the general case can be found from Bryan. But if  $m=m_1$  or  $m_2$  or  $m_3$  or  $m_4$  i.e. if the period of the gust becomes identically equal to one of the periods of natural oscillations of the system then  $F(m)=0$  and  $u_0, v_0$  and  $\epsilon_0$  would become infinitely great unless  $\phi(m)$ ,  $\psi(m)$  and  $\chi(m)$  become zero at the same time i.e. unless  $\phi(m)$  and  $F(m)$ ,  $\psi(m)$  and  $F(m)$ ,  $\chi(m)$  and  $F(m)$  have common roots.

$$\text{Now } F(m) = A_0 m^4 + B_0 m^3 + C_0 m^2 + D_0 m + E_0$$

$$\phi(m) = Am^3 + Bm^2 + Cm + D \text{ (say)}$$

If  $F(m)$  and  $\phi(m)$  have a common factor to find a relation between the coefficients of the two equations we follow Sylvester's Dialytic method of elimination. Now suppose certain value of  $m$  make both  $F(m)$  and  $\phi(m)$  zero i.e.

$$A_0 m^4 + B_0 m^3 + C_0 m^2 + D_0 m + E_0 = 0 \quad \dots (1)$$

$$Am^3 + Bm^2 + Cm + D = 0 \quad \dots (2)$$

Let us consider the different powers of  $m$  as so many distinct unknowns. We have then 2 non-homogenous linear equations in the four unknowns  $m, m^2, m^3, m^4$ . Multiplying (1) by  $m$  and then by  $m^2$  and (2) by  $m, m^2, m^3$  in turn we have

$$A_0 m^5 + B_0 m^4 + C_0 m^3 + D_0 m^2 + E_0 m = 0$$

$$A_0 m^5 + B_0 m^4 + C_0 m^3 + D_0 m^2 + E_0 m = 0$$

$$A_0 m^4 + B_0 m^3 + C_0 m^2 + D_0 m + E_0 = 0$$

$$Am^4 + Bm^3 + Cm^2 + Dm = 0$$

$$Am^4 + Bm^3 + Cm^2 + Dm = 0$$

$$Am^5 + Bm^4 + Cm^3 + Dm^2 = 0$$

$$Am^5 + Bm^4 + Cm^3 + Dm^2 = 0$$

a system of seven non-homogenous, linear equations in six unknowns.

If  $m$  satisfy (1) and (2) it will evidently satisfy all the above equations. These equations are therefore consistent. Hence eliminating  $m^6, m^5, m^4, m^3, m^2, m$ , we get as a necessary condition for (1) and (2) to have a common root

$$\begin{vmatrix} A_0 & B_0 & C_0 & D_0 & E_0 & 0 & 0 \\ 0 & A_0 & B_0 & C_0 & D_0 & E_0 & 0 \\ 0 & 0 & A_0 & B_0 & C_0 & D_0 & E_0 \\ 0 & 0 & 0 & A & B & C & D \\ 0 & 0 & A & B & C & D & 0 \\ 0 & A & B & C & D & 0 & 0 \\ A & B & C & D & 0 & 0 & 0 \end{vmatrix} = 0$$

In order to avoid algebraic complications at the outset, we first consider a single lifting plane propelled horizontally by a central thrust. Two surfaces  $S_1, S_2$  of which the front surface  $S_1$  supports the whole weight of the aeroplane being inclined to the line of flight at an angle  $\alpha$ , while the rear surface  $S_2$  acts as a tail or rudder or auxiliary plane, being placed in a neutral direction (so that  $\alpha_2 = 0$ ). Distance between the centres of pressure of the two planes is  $l$ , the line of action of the propellor thus passes through the centre of gravity of the machine; the direction of the thrust being along the line of flight is horizontal. The values of the nine derivations  $X_u \dots N_v$  are given by Bryan in this case as follows :

$$\begin{aligned} X_u &= 2KS_1 U \sin^2 \alpha, & X_v &= KS_1 U \sin \alpha \cos \alpha, & X_w &= 0 \\ Y_u &= 2KS_1 U \sin \alpha \cos \alpha, & Y_v &= KS_1 U \cos^2 \alpha + KS_2 U, & Y_w &= -KS_2 U l \\ N_u &= 0, & N_v &= -KS_2 M l, & N_w &= KS_2 U l^2 \end{aligned}$$

where  $K$  is the coefficient of resistance of the plane.

Hence we obtain in the case when the machine is descending with velocity  $U$  at an angle  $\theta$  with the horizontal

$$A_0 = CW^2$$

$$B_0/gU = CWK[S_1(1 + \sin^2 \alpha) + S_2] + W^2 KS_2 l^2$$

$$C_0/g^2 U^2 = 2CK^2 S_1 S_2 \sin^2 \alpha + WK^2 S_1 S_2 l^2 (1 + \sin^2 \alpha) + \frac{W^2}{g} KS_2 l^2$$

$$D_0/g^3 U^3 = \frac{W}{g} (K^2 S_1 S_2 l \sin \alpha \cos \alpha \cdot 2 \tan \alpha + \tan \theta)$$

$$E_0/g^4 U^4 = \frac{2W}{g U^2} K^2 S_1 S_2 l \sin \alpha \cos (\alpha - \theta)$$

and for  $u_0$

$$A = \frac{CW}{g^2} P$$

$$B = [CKS_1 U \cos^2 \alpha + CKS_2 U + WKS_2 U l^2] \frac{P}{g} - CKS_1 U \sin \alpha \cos \alpha \cdot \frac{Q}{g}$$

$$C = \left[ K^2 S_1 S_2 U^{3/2} \cos^2 \alpha + \frac{W}{g} KS_2 U^{1/2} \right] P - K^2 S_1 S_2 U^{3/2} \sin \alpha \cos \alpha \cdot Q$$

$$+ \left[ KS_1 U \sin \alpha \cos \alpha \left( \frac{WU}{g} - KS_2 U l \right) + \frac{W^2}{g} \cos \theta \right] R$$

$$D = KS_2 U l W \sin \theta \cdot P + KS_2 U l W \cos \theta \cdot Q$$

$$+ [KS_1 U \sin \alpha \cos \alpha W \sin \theta + W \cos \theta (KS_1 U \cos^2 \alpha + KS_2 U)] R$$

and for the equation of equilibrium  $W \cos \theta = KS_1 U^2 \sin \alpha \cos \alpha$

The quantities  $P$ ,  $Q$ ,  $R$  that we have assumed for the resolved parts of the magnitude of the gust will have a relation among themselves like  $aP = bQ = cR$  where  $a$ ,  $b$ ,  $c$  in the general case are functions of time.

#### CASE 1.

In this case we shall assume that  $a = b = c = 1$ ,  $\theta = 0$  i.e. the machine is flying horizontally and  $\alpha$  a small quantity so that  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$  are neglected. Then

$$A_0 = CW^2$$

$$B_0/gU = CWK(S_1 + S_2) + W^2 KS_2 l^2$$

$$C_0/U^2 g^2 = WKS_1 S_2 l^2 + \frac{W^2}{g} KS_2 l$$

$$D_0/U^3 g^3 = 0$$

$$E_0/g^4 U^4 = \frac{2W}{U^2 g} K^2 S_1 S_2 l \sin \alpha \cos \alpha$$

and for the equation of equilibrium  $W = KS_1 U^2 \sin \alpha \cos \alpha$   
and

$$A = \frac{CW}{g} P$$

$$B = \frac{PKU}{g} [CS_1(1 - \cos \alpha \sin \alpha) + S_2(C + Wl^2)]$$

$$C = P \left[ K^2 S_1 S_2 U^2 l^2 (1 - \cos \alpha \sin \alpha) + K^2 S_1 S_2^2 U^2 l \sin \alpha \cos \alpha \right. \\ \left. \left( \frac{U^2}{g} - 1 \right) + 2 \frac{W^2}{g} \right]$$

$$D = PWKU(S_2 l + S_1 + S_2)$$

Then expanding the Sylvester's Determinant and remembering that  $W = KS_1 U^2 \sin \alpha \cos \alpha$  for the condition of equilibrium and neglecting  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$ , we find that the determinant reduces to zero i.e.  $\phi(m)$  and  $F(m)$  have a common factor between them.

Now  $n_0 = \frac{\phi(m)}{F(m)}$  and even if  $m = m_1$  i.e. if a period of the gust

coincide with a period of the natural oscillation of the system,  $n_0$  will not tend to become infinitely great i.e. the forced oscillation would not make the system unstable for that particular period of the gust.

We have arrived at this particular result by assuming  $\alpha$  small i.e. by neglecting  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$ . Bryan has shown that the natural oscillation of the system that result from the above assumption gives the short oscillations of the aeroplane. Hence if the period of the gust of wind coincide with the period of the small oscillations of the aeroplane it will have no effect in violently disturbing the stability of the system so far as the velocity  $u$  is concerned. Hence  $u = a_1 e^{m_1 t} + a_2 e^{m_2 t} + a_3 e^{m_3 t} + a_4 e^{m_4 t} + u_0 e^{m t}$  gives the natural and forced oscillations of the system in the direction of its motion so far as the short oscillation are concerned. The case when the period of the gust coincides with the periods of the long or slow oscillations we can no longer neglect  $\sin^2 \alpha$  only and we shall take it up afterwards first finishing the examination of the effect on  $v_0$  and  $\epsilon_0$ . The case of  $v_0$  is quite similar to that of  $u_0$  but  $\epsilon_0$  both because it is an angle whose great variation may very well become dangerous to the aeroplane and

it presents quite a different type of equations for  $\chi^{(m)}$ , will give some interesting results. We have

$$\epsilon_0 = \frac{\chi^{(m)}}{F^{(m)}} \text{ where}$$

$$\chi^{(m)} = P \begin{vmatrix} \frac{W}{g} m + X_{11} & X_{12} & 1 \\ Y_{21} & \frac{W}{g} m + Y_{22} & 1 \\ N_{31} & N_{32} & 1 \end{vmatrix} = Am^2 + Bm + C$$

$$A = P \frac{W^2}{g^2}, B = -P \frac{W}{g} (X_{11} + Y_{22}), C = P[(Y_{21}N_{32} - N_{31}Y_{22}) - (X_{11}N_{32} - X_{12}N_{31}) - X_{12}Y_{21}]$$

Hence

$$A_0 = CW^2$$

$$B_0/gU = CWK(S_1 + S_2) + W^2KS_2/l^2$$

$$C_0/g^2U^2 = WKS_1S_2/l + \frac{W^2}{g}KS_2/l$$

$$D_0 = 0 \quad E_0/g^2U^2 = \frac{2W}{gl^{\frac{3}{2}}}K^2S_1S_2l \sin \alpha \cos \alpha$$

and

$$A = P \frac{W^2}{g^2}, B = P \frac{W}{g}KS_2U/l, C = -2PK^2S_1S_2U^2/l \sin \alpha \cos \alpha$$

If a period of the gust of wind be equal to the natural period of oscillation of the aeroplane then  $m = m_1$  and to find the condition that  $F(m)$  and  $\chi^{(m)}$  may have a common factor. The equations are

$$Am^2 + B_0m^2 + C_0m^2 + D_0m + E_0 = 0$$

$$Am^2 + Bm + C = 0$$



The condition these two equations have a common root is given by Bôcher as follows :

The resultant R of the two equations must be zero i.e.

$$R = \begin{vmatrix} A_0 & B_0 & C_0 & D_0 & E_0 & 0 \\ 0 & A_0 & B_0 & C_0 & D_0 & E_0 \\ 0 & 0 & 0 & A & B & C \\ 0 & 0 & A & B & C & 0 \\ 0 & A & B & C & 0 & 0 \\ A & B & C & 0 & 0 & 0 \end{vmatrix} = 0$$

Expanding R and remembering that  $W = KS_1 U^2 \sin a \cos a$  and neglecting terms containing  $\sin^2 a$  and higher powers of  $\sin a$  we see that  $R=0$  i.e.,  $F(m)$  and  $\chi(m)$  have a common factor between them. Thus

$$\epsilon = \epsilon_1 e^{m_1 t} + \epsilon_2 e^{m_2 t} + \epsilon_3 e^{m_3 t} + \epsilon_4 e^{m_4 t} + \epsilon_0 e^{m t}$$

represents oscillatory motions in all cases except when  $m$  coincides with those values of the roots of  $F(m)=0$  that give slow oscillations of the system. Now since  $F(m)$  and  $\chi(m)$  have a common factor corresponding to that value of  $m=m_1$  which gives the short oscillations of the system, the degree of that common factor is two, hence it is proportional

to  $\chi(m)$  i.e.  $F(m) = \chi(m)F_1(m)$  and  $\epsilon_0 = \frac{n}{F_1(m)}$ ; those two values of  $m$

that make  $F_1(m)=0$  will make  $\epsilon_0$  infinitely great i.e., make the motion of the aeroplane unstable. Hence those values of  $m$  corresponding to the long oscillations of the system will give the aeroplane a pitching tendency which may prove dangerous.

In the case of  $u_0$  and  $v_0$  when  $\sin^2 a$  does not vanish we see that the Sylvester's Determinant does not vanish i.e.  $F(m)$  and  $\phi(m), \psi(m)$  have not a common root. Therefore when the period of the gust coincides with that of the slow oscillations of the system  $u_0$  and  $v_0$  become very great but this fact by itself could not have given the machine any instability. It is only when we have considered the value of  $\epsilon_0$  in this case and find as above that it also is very great we conclude that the forced oscillations in this case assume dangerous proportion.

Hence in the case when the machine is flying horizontally the effect of a periodic gust of wind will be only to superimpose another oscillation on the system (provided the machine has inherent stability) for all periods of its gust except when it synchronises with the long oscillations of the aeroplane.

## CASE II.

In this case we still assume  $a=b=c=1$  but  $\theta \neq 0$  i.e. the machine is descending at an angle  $\theta$  to the horizontal and for purposes of approximation and algebraic simplifications we shall suppose  $\theta$  and  $\alpha$  both small so that  $\cos(\theta - \alpha)$  may be taken equal to unity, then

$$A_0 = CW^2$$

$$B_0/gU = CWK[S_1(1 + \sin^2 \alpha) + S_2] + W^2 KS_2 l^2$$

$$C_0/g^2 U^2 = 2CK^2 S_1 S_2 \sin^2 \alpha + WK^2 S_1 S_2 l^2 (1 + \sin^2 \alpha) + \frac{W^2}{g} KS_2 l$$

and for  $D_0$  and  $E_0$  we must go to the equations for  $u_0$ ,  $v_0$  and  $\epsilon_0$  in which substituting the values of  $X_1, X, \dots, N_r$ , we get

$$\left( W \frac{m}{g} + 2KS_1 U \sin^2 \alpha \right) u_0 + KS_1 U \sin \alpha \cdot v_0 - W \cos \theta \cdot \epsilon_0 + P = 0$$

$$2KS_1 U \sin \alpha \cos \alpha \cdot u_0 + \left( W \frac{m}{g} + KS_1 U \cos^2 \alpha + KS_2 U \right) v_0$$

$$+ \left[ \left( W \frac{U}{g} - KS_2 U l \right) m + W \sin \theta \right] \epsilon_0 + P = 0$$

$$0 - KS_2 U l \cdot v_0 + \left( \frac{C}{g} m^2 + KS_2 U l^2 m v \right) \epsilon_0 + P = 0$$

Hence

$$D_0/g^2 U^2 = \frac{2W}{g} K^2 S_1 S_2 l \sin^2 \alpha + \frac{W^2}{g U^2} KS_2 l \sin \theta$$

$$E_0/g^2 U^2 = \frac{2W}{g U^2} K^2 S_1 S_2 l [\sin \alpha \cos \alpha \cos \theta + \sin^2 \alpha \sin \theta]$$

From the equations of equilibrium  $W \cos \theta = K S_1 U^2 \sin \alpha \cos \alpha$  these reduce to

$$D_0/g^3 U^3 = \frac{W}{g} K^2 S_1 S_2 l \sin \alpha \cos \alpha (2 \tan \alpha + \tan \theta)$$

$$E_0/g^4 U^4 = \frac{2W}{U^2 g} K^2 S_1 S_2 l \sin \alpha \cos (\theta - \alpha)$$

If now we neglect  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$

$$A_0 = CW^2$$

$$B_0/gU = CWK(S_1 + S_2) + W^2 K S_2 l^2$$

$$C_0/g^3 U^3 = WK^2 S_1 S_2 l^2 + \frac{W^2}{g} K S_2 l$$

$$D_0/g^3 U^3 = \frac{W}{g} K^2 S_1 S_2 l \sin \alpha \cos \alpha \tan \theta$$

$$E_0/g^4 U^4 = \frac{2W}{U^2 g} K^2 S_1 S_2 l \sin \alpha$$

We see that  $A_0$ ,  $B_0$ ,  $C_0$  and  $E_0$  are the same in this case as in Case I and in  $\chi(m)$ ,  $\theta$  does not enter, hence  $\epsilon_0$  finite for those values of  $m$  that do not coincide with a root of  $F(m) = 0$  giving the slow oscillation of the system.

But in the case of  $\nu_0$

$$\Lambda = C \frac{W}{g^2} \cdot P$$

$$B = \frac{PKU}{g} [CS_1(1 - \cos \alpha \sin \alpha) + S_2(C + Wl^2)]$$

$$C = P \left[ K^2 S_1 S_2 U^2 l^2 (1 - \sin \alpha \cos \alpha) + \frac{W}{g} KU^2 (S_2 l - S_1 \sin \alpha \cos \alpha) \right. \\ \left. - K^2 S_1 S_2 U^2 l \sin \alpha \cos \alpha + \frac{W}{g} K S_1 U^2 \sin \alpha \cos \alpha \right]$$

$$= P \left[ K^2 S_1 S_2 U^2 l^2 (1 - \sin^2 \alpha \cos \alpha) - K^2 S_1 S_2 U^2 l \sin^2 \alpha \cos \alpha + \frac{W}{g} \right. \\ \left. K S_2 U^2 l \right]$$

$$D = PKU [(S_2 l + S_1 \sin \alpha \cos \alpha) W \sin \theta + (S_2 l + S_1 + S_2) W \cos \theta]$$

and the equation of equilibrium  $W \cos \theta = K S_1 U^2 \sin \alpha \cos \alpha$ . We find on expanding  $R$  that it does not vanish even when  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$  are neglected. Hence in this case the machine is distinctly unstable for the forced oscillations corresponding to either periods of natural oscillations.

### Group II.

At the onset in this group we start with the assumption that  $P' = Q' = R' =$  a constant quantity which is conveniently taken as unity.

To solve this group of equations we assume  $w, p, q$ , each proportional to  $w_0 e^{mt}$ ,  $p_0 e^{mt}$ ,  $q_0 e^{mt}$ , so that  $\frac{dw}{dt} = w_0 m e^{mt}$ ,  $\frac{dp}{dt} = p_0 m e^{mt}$ ,  $\frac{dq}{dt} = q_0 m e^{mt}$ . Hence substituting these in this group and eliminating  $e^{mt}$  we get

$$\left( \frac{W}{g} m + Z_u \right) w_0 + \left( \frac{W}{m} \cos \theta + Z_p \right) p_0 \\ + \left( -W \frac{U}{g} - \frac{W}{m} \sin \theta + Z_q \right) q_0 + R' = 0$$

$$L_u \cdot w_0 + \left( \frac{A}{g} m + L_p \right) p_0 + \left( -F \frac{m}{g} + L_q \right) q_0 + P' = 0$$

$$M_u \cdot w_0 + \left( -F \frac{m}{g} + M_p \right) p_0 + \left( B \frac{m}{g} + M_q \right) q_0 + Q' = 0$$

on the following identity  $m \phi \cos \theta = p \cos \theta - q \sin \theta$ .

Solving these equations for  $w_0$ ,  $p_0$ ,  $q_0$  and putting  $P'=Q'=R' = 1$

$$\begin{array}{c}
 \begin{array}{ccc}
 \frac{W}{m} \cos \theta + Z_p, -W \frac{U}{g} - \frac{W}{m} \sin \theta + Z_p, & 1 \\
 A \frac{m}{g} + L_p, & -F \frac{m}{g} + L_s, & 1 \\
 -F \frac{m}{g} + M_p, & B \frac{m}{g} + M_s, & 1 \\
 -p_0
 \end{array} \\
 = \\
 \begin{array}{ccc}
 W \frac{m}{g} + Z_w, -W \frac{U}{g} - \frac{W}{m} \sin \theta + Z_q, & 1 \\
 L_w, & -F \frac{m}{g} + L_s, & 1 \\
 M_w, & B \frac{m}{g} + M_s, & 1 \\
 q_0
 \end{array} \\
 = \\
 \begin{array}{ccc}
 W \frac{m}{g} + Z_w, & \frac{W}{m} \cos \theta + Z_p, & 1 \\
 L_w, & A \frac{m}{g} + L_p, & 1 \\
 M_w, & -F \frac{m}{g} + M_p, & 1 \\
 -1
 \end{array} \\
 = \\
 \begin{array}{ccc}
 W \frac{m}{g} + Z_w, & \frac{W}{m} \cos \theta + Z_p, -W \frac{U}{g} - \frac{W}{m} \sin \theta + Z_s, \\
 L_w, & A \frac{m}{g} + L_p, & -F \frac{m}{g} + L_s, \\
 M_w, & -F \frac{m}{g} + M_p, & B \frac{m}{g} + M_s,
 \end{array}
 \end{array}$$

Hence

$$w_0 = \frac{Am^3 + Bm^2 + Cm + D}{A_1 m^4 + B_1 m^3 + C_1 m^2 + D_1 m + E_1}$$

where

$$A_1 = W(AB - F^2)$$

$$B_1/g = Z_q(AB - F^2) + W[AM_q + BL_p + F(L_q + M_p)]$$

$$C_1/g^2 = Z_w[AM_q + BL_p + F(L_q + M_p)] + W(L_p M_q - L_q M_p)$$

$$- Z_p(FM_w + BL_w) - \left( Z_q - W \frac{U}{g} \right) (FL_w + AM_w)$$

$$D_1/g^3 = Z_w(L_p M_q - L_q M_p) + Z_p(L_q M_w - M_q L_w)$$

$$+ \left( Z_q - W \frac{U}{g} \right) (L_w M_p - L_p M_w)$$

$$+ \frac{W}{g} [(FL_w + AM_w) \sin \theta - (BL_w + FM_w) \cos \theta]$$

$$E_1/g^4 = \frac{W}{g} [(L_q M_p - M_q L_w) \cos \theta - (L_w M_p - M_w L_p) \sin \theta]$$

and

$$A = \frac{AB - F^2}{g^2}$$

$$B = \frac{1}{g} \left[ A(M_q - Z_q) + B(L_p - Z_q) + F(L_q - Z_q) + F(M_p - Z_p) \right. \\ \left. + W \frac{U}{g} (A + F) \right]$$

$$C = (L_p M_q - L_q M_p) + (Z_p L_q - Z_q L_p) + (M_p Z_q - M_q Z_p)$$

$$+ W \frac{U}{g} (L_p - M_p) + \frac{W}{g} [(A + F) \sin \theta - (B + F) \cos \theta]$$

$$D = W \cos \theta (L_q - M_q) + W \sin \theta (L_p - M_p).$$

Also

$$P_0 = \frac{A'm^3 + B'm^2 + C'm + D'}{A_1 m^4 + B_1 m^3 + C_1 m^2 + D_1 m + E_1}$$

where

$$A' = (B + F) \frac{W}{g^2}$$

$$B' = \frac{1}{g} [B(Z_{\pi} - L_{\pi}) + F(Z_{\pi} - M_{\pi}) + W(M_{\eta} - L_{\eta})]$$

$$C' = (L_{\eta} M_{\pi} - L_{\pi} M_{\eta}) + (M_{\eta} Z_{\pi} - M_{\pi} Z_{\eta}) + (L_{\pi} Z_{\eta} - Z_{\pi} L_{\eta})$$

$$+ W \frac{L}{g} (M_{\pi} - L_{\pi})$$

$$D' = (M_{\pi} - L_{\pi}) W \sin \theta.$$

Also

$$A'' = (A + F) \frac{W}{g^2}$$

$$B'' = \frac{1}{g} [A(Z_{\pi} - M_{\pi}) + F(Z_{\pi} - L_{\pi}) + W(L_{\eta} - M_{\eta})]$$

$$C'' = (L_{\pi} M_{\eta} - L_{\eta} M_{\pi}) + (M_{\pi} Z_{\eta} - Z_{\pi} M_{\eta}) + (Z_{\pi} L_{\eta} - L_{\pi} Z_{\eta})$$

$$D'' = (M_{\pi} - L_{\pi}) W \cos \theta$$

and

$$q_0 = \frac{A'' m^3 + B'' m^3 + C'' m + D''}{A_1 m^4 + B_1 m^3 + C_1 m^2 + D_1 m + E_1}$$

#### CASE I.—STRAIGHT PLANES

By this we mean planes perpendicular to the plane of  $x-y$  with no vertical fins. In this case we get from Bryan Art. 77  $Z_{\pi}$ ,  $Z_{\eta}$ ,  $L_{\pi}$ ,  $M_{\pi}$ , each = zero. Thus we find that  $D_1 = 0$ ,  $E_1 = 0$  and for straight planes  $C_1 = 0$  (but in this case the original motion is unstable so we neglect it). If there are 2 planes whose angles of attack are  $\alpha_1$  and  $\alpha_2$  and the moments of inertia about the plane  $x-y$  be  $I_1$  and  $I_2$  we find

$$\frac{C_1}{K^2 U^2 g^2} = 2W I_1 I_2 \sin^2(\alpha_1 - \alpha_2)$$

But even in this case 2 roots of the biquadratic are zero which indicates lack of inherent stability, so we neglect this case altogether.

## CASE II.

Now at once let us go to the system that is most stable and whose range of stability is great. This is the system with 2 raised fins at the same height. In this case we take 2 fins  $T_1$  and  $T_2$  (of total area  $T$ ) one in front and other in the rear of the C. G. of the system and both above the  $x$ -axis in the  $x$ - $y$  plane with the  $y$  of the C. P. equal and their joint C. P. in a line through the C. G. of the system perpendicular to the main planes. In this case, Bryan has shown, Art. 84, that the machine has inherent stability. Now to find the effect of the periodic gust on such a system.

Let  $(x, y)$  be the co-ordinates of the centre of mean position (or centre of pressure) of the 2 fins, and  $M_1, M_2, P$  the moments and the products of inertia of the areas of the fins with respect to axes parallel to the co-ordinate axes through  $(x, y)$  we get from Bryan since  $M_1 = P = 0$ , in this case for the fins

$$Z_w = K^1 TU, \quad Z_p = K^1 TUy, \quad Z_q = -K^1 TUx$$

$$L_w = K^1 TUy, \quad L_p = K^1 TUy^2, \quad L_q = -K^1 TUxy$$

$$M_w = -K^1 TUx, \quad M_p = -K^1 TUxy, \quad M_q = K^1 U(Tx^2 + M_2)$$

and by Lanchester's 'Fin Resolution'  $M_2 = \frac{T_1 T_2}{T_1 + T_2} \times (\text{distance between fins})^2$ .

For simplification of algebra let us assume that  $K^1 = K$  i.e. the coefficients of resistance of the fins and the main planes are equal.

Also let us assume  $\alpha$  small, so that  $x=0$  and also  $F=0$  i.e. the  $x$ -axis is a principal axis. Then

$$Z_w = KTU, \quad Z_p = KUTy, \quad Z_q = 0$$

$$L_w = KTUy, \quad L_p = KUTy^2, \quad L_q = 0$$

$$M_w = 0, \quad M_p = 0, \quad M_q = KUM_2$$

Also let us first consider the case when  $\theta=0$  i.e. the machine is flying horizontally.



The above are the resistance derivatives due to the 2 fins only, the resistance derivatives for a main plane at an angle  $\alpha$  and a rudder plane are

$$Z_w=0, \quad Z_p=0, \quad Z_q=0$$

$$L_w=0, \quad L_p=KUI \cos^2 \alpha, \quad L_q=-2KUI \sin \alpha \cos \alpha$$

$$M_w=0, \quad M_p=-KUI \sin \alpha \cos \alpha, \quad M_q=2KUI \sin^2 \alpha$$

so that the whole resistance derivatives are, neglecting  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$

$$Z_w=KTU, \quad Z_p=KUTy, \quad Z_q=0$$

$$L_w=KUTy, \quad L_p=KUTy^2, \quad L_q=2KUI \tan \alpha$$

$$M_w=0, \quad M_p=-KUI \sin \alpha \cos \alpha, \quad M_q=KUM,$$

and

$$A_1=ABW$$

$$B_1/gKU=W(AM_s+BTy^2)$$

$$C_1/g^2K^2U^2=TM_s(\Delta+Wy^2)$$

$$D_1/g^2K^2U^2=\frac{W}{g}[Iy \cdot T \cdot \tan \alpha - B \cdot T \cdot Y/K^2U^2]$$

$$E_1/g^2K^2U^2=-\frac{W}{g} \cdot Y \cdot T \cdot M_s/K^2U^2$$

and for  $p_0$

$$\Delta'=\frac{BW}{g^2}$$

$$B'/KU=\frac{1}{g}[BT(1-y)+W(M_s+2I \tan \alpha)]$$

$$C'/K^2U^2=TM_s(1-y)+2IT \tan \alpha - \frac{W}{kg} T \cdot y \cdot$$

$$D'=0$$

Using these quantities in the Sylvester's Determinant and remembering that  $W=KS_1U^2 \sin \alpha \cos \alpha$  we find on developing and neglecting terms containing  $\sin^2 \alpha$  and higher powers of  $\sin \alpha$ , that the determinant vanishes i.e. the two equations

$$A_1m^4+B_1m^3+C_1m^2+D_1m+E_1=0$$

$$A'm^3+B'm^2+C'm+D'=0$$

have a common root between themselves. Now since  $D'=0$  the last equation reduces to  $A'm^2+B'm+C'=0$  and it will have two imaginary roots if  $y$  be negative, which is one of the conditions of the inherent stability of the machine. Also we know that there is only one type of lateral oscillation of the system i.e.  $A_1m^2+B_1m^2+C_1m^2+D_1m+E_1=0$  has only a pair of imaginary roots and since a period of the gust is to coincide with a period of the oscillation of the aeroplane it must coincide with this particular root. Thus we see that the forced lateral oscillation is never unstable in the case of  $p_0$  when the machine is flying horizontally and we can neglect  $\sin^2\alpha$  and higher powers of  $\sin \alpha$ . The same conclusion holds good in the case of  $w_0$  and  $q_0$ .

Hence we conclude that when the plane is flying horizontally and  $\alpha$  is such that  $\sin^2\alpha$  and higher powers of  $\sin \alpha$  are negligible the effect of a periodic gust of wind on lateral motion is only to superimpose another oscillation which never becomes dangerous.

### CASE III.

In this we assume  $\theta \neq 0$  but we neglect  $\sin^2\alpha$  and higher powers of  $\sin \alpha$  then

$$A_1=ABW$$

$$B_1/KUg=W(AM_2+BTy^2)$$

$$C_1/K^2U^2g^2=TM_2(A+Wy^2)$$

$$D_1/K^2U^2g^2=\frac{W}{g}[yIT \tan \alpha - BTy \cos \theta / K^2U^2]$$

$$E_1/K^2U^2g^2=-\frac{W}{g}\frac{y}{K^2U^2}-TM_2 \cos \theta$$

Thus we see that  $\theta$  comes only in the form of cosine and that only in  $D_1$  and  $E_1$ .

If we consider the case of  $p_0$ ,  $A'$ ,  $B'$ ,  $C'$  remain the same as before only  $D'=-KUTy \cdot W \sin \theta$ ; so also in  $q_0$  only change is in  $D''$  which becomes  $D''=-KUTyW \cos \theta$  and in  $w_0$ ,  $A$  and  $B$  remain the same  $C$  and  $D$  change so that

$$\begin{aligned} C &= K^2U^2M_2Ty(y-1)-2K^2U^2TyI \tan \alpha + \frac{W}{g} KU^2Ty^2 \\ &\quad + \frac{W}{g} (A \sin \theta - B \cos \theta) \end{aligned}$$

$$D=KU(Ty^2 \sin \theta - M_2 \cos \theta) W.$$

Now substituting these values in the Sylvester's Determinant for  $w_0 p_0$  and  $q_0$  and remembering that  $W \cos \theta = K S_1 U^2 \sin a \cos a$  we find on expanding that the determinant does not vanish in any of the cases. Hence when the period of the gust coincides with the period of the system the forced oscillations become very great.

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# ON A FACTORABLE CONTINUANT

By

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Some factorable continuants have been discovered by such eminent mathematicians as Painvin,<sup>1</sup> Sylvester,<sup>2</sup> Metzler,<sup>3</sup> Muir<sup>4</sup> and Datta.<sup>5</sup> The present paper contains a continuant of the same class which has been derived from a finite series with the help of Heilermann's Theorem.<sup>6</sup> This continuant has been evaluated determinantly and some algebraic relations *viz.*, theorems (1), (2), (8), (9), (11), (12), (13), (14), (15) and (24) have been deduced. In converting the finite series to a continued fraction, we have come to a kind of determinants whose numerators and denominators are both resolvable into a number of binomial factors.<sup>7</sup>

<sup>1</sup> Painvin, (1858). "Sur uncertain systeme d'equations lineaires." *Journ. de Math.* (2) III, pp. 41-46; or The Theory of Determinants in the Historical Order of Development by Muir T., Vol. 2, pp. 422-434.

<sup>2</sup> Sylvester J. J. (1854) "Theoreme sur les determinants de M. Sylvester." *Nouv Annales de Math.*, xiii, p. 305, or The Theory of Determinants in the Historical Order of Development by Muir T., Vol. 2, p. 425.

<sup>3</sup> W. H. Metzler. "Some factorable continuants," *Edin. Proc. Roy. Soc.*, 34, 1914 (223-229).

<sup>4</sup> Muir T. "Continuants resolvable into linear factors" *Trans. Edin. Roy. Soc.*, 41, 1905 (343-358). Muir T. "Factorizable continuants" *Trans. S. Afric. Philos. Soc.*, 15 pt. 1, 1904 (29-33).

<sup>5</sup> Haripada Datta, "On the Failure of Heilermann's Theorem." *Proc. Edin. Math. Soc.* Vol. 35. "On the Theory of Continued Fractions" *Proc. Edin. Math. Soc.*, Vol. 34.

<sup>6</sup> *Journal für Math.* 33 (1845), p. 174.

<sup>7</sup> Cauchy, (1841) "Mémoire sur les fonctions alternées et sur les sommes alternées," *Exercices d'analyse et de Phys. Math.*, II, pp. 151-159, or The Theory of determinants in the Historical Order of Developments by Muir T., Vol. I, pp. 342-345.

1.<sup>1</sup>

$$\begin{aligned}
& \{(1+y)(1+ay)(1+a^2y)\dots(1+a^{r-1}y)\} \\
& \equiv \{(y-\delta)(ay-\delta)(a^2y-\delta)\dots(a^{r-1}y-\delta)\} \\
& + {}^rS_1(1+\delta)\{(y-\delta)(ay-\delta)\dots(a^{r-2}y-\delta)\} \\
& + {}^rS_2\left(\frac{1}{a} + \delta\right)(1+\delta)\{(y-\delta)(ay-\delta)\dots(a^{r-3}y-\delta)\} + \dots \\
& + {}^rS_r\left\{\left(\frac{1}{a^{r-1}} + \delta\right)\left(\frac{1}{a^{r-2}} + \delta\right)\dots(1+\delta)\right\} \quad \dots \quad (1)
\end{aligned}$$

where  ${}^rS_p$  denotes the sum of the products of  $r$  factors  $1, a, a^2, \dots, a^{r-1}$  taken  $p$  of them at a time.

*Proof.* Let us take the series

$$\begin{aligned}
& (a+\delta)(a^2+\delta)(a^3+\delta), \quad (1+\delta)(a+\delta)(a^2+\delta), \\
& \left(\frac{1}{a} + \delta\right)(1+\delta)(a+\delta), \quad \left(\frac{1}{a^2} + \delta\right)\left(\frac{1}{a} + \delta\right)(1+\delta)\dots
\end{aligned}$$

and obtain from it  $\Delta_1, \Delta_2$  etc., the successive orders of differences by using  $1, a, a^2 \dots$  as multipliers (see Art 5, Paper 3).

Then we shall find that in this particular case where there are three factors in each term of the original series, each term of  $\Delta_k$  and higher orders of differences vanishes. So by Art 5 (i), Paper 3 we have

$$\begin{aligned}
& (a+\delta)(a^2+\delta)(a^3+\delta) - {}^1S_1(1+\delta)(a+\delta)(a^2+\delta). \\
& + {}^2S_2\left(\frac{1}{a} + \delta\right)(1+\delta)(a+\delta) - \dots \\
& + (-1)^k {}^kS_k\left(\frac{1}{a^{k-1}} + \delta\right)\left(\frac{1}{a^{k-2}} + \delta\right)\left(\frac{1}{a^{k-3}} + \delta\right) = 0, \text{ where } k = \text{or} > 4.
\end{aligned}$$

Thus generally we have

$$\begin{aligned}
& \{(a+\delta)(a^2+\delta)\dots(a^{r-1}+\delta)\} - {}^1S_1\{(1+\delta)(a+\delta)\dots(a^{r-2}+\delta)\} \\
& + {}^2S_2\left\{\left(\frac{1}{a} + \delta\right)(1+\delta)\dots(a^{r-3}+\delta)\right\} - \dots \\
& + (-1)^k {}^kS_k\left\{\left(\frac{1}{a^{k-1}} + \delta\right)\left(\frac{1}{a^{k-2}} + \delta\right)\dots(a^{r-k-1}+\delta)\right\} = 0 \quad \dots \quad (2)
\end{aligned}$$

where  $k = \text{or} > r$ .

<sup>1</sup> cf. "On the Evaluation of Some Factorable Continuants," Part II, Art 2. *Bul. Cal. Math. Soc.*, Vol. XIV, pp. 91-106. In subsequent references, this paper will be called Paper 3.

If the original series be  $1, 1, 1, \dots$ , then each term of  $\Delta_1, \Delta_2, \dots$  is zero. Hence we have

$$1 - {}^k S_1 + {}^k S_2 - \dots + (-1)^k {}^k S_k = 0$$

where  $k = \text{or} > 1$ .

Let us now take the particular case of the theorem (1) when  $r=3$  viz.,

$$\begin{aligned} (1+y)(1+ay)(1+a^2y) &\equiv (y-\delta)(ay-\delta)(a^2y-\delta) \\ &+ {}^3S_1(1+\delta)(y-\delta)(ay-\delta) + {}^3S_2\left(\frac{1}{a} + \delta\right)(1+\delta)(y-\delta) \\ &+ {}^3S_3\left(\frac{1}{a^2} + \delta\right)\left(\frac{1}{a} + \delta\right)(1+\delta). \end{aligned} \quad \dots (4)$$

If we substitute  $\delta, -1, -\frac{1}{a}$  or  $-\frac{1}{a^2}$  for  $y$  in (4), we can show by (2) and (3) that for each substitution the equation (4) is satisfied. Hence it is an identity. The general case may be similarly treated.

*Ex. 1.*

$$\begin{aligned} &\left[ \begin{matrix} r \\ 1 \end{matrix} \right] - a(1+y)\left[ \begin{matrix} r \\ 2 \end{matrix} \right] + a^2(1+y)(1+ay)\left[ \begin{matrix} r \\ 3 \end{matrix} \right] \\ &\quad - a^3(1+y, 1+a^2y)\left[ \begin{matrix} r \\ 4 \end{matrix} \right] + a^4(1+y, 1+a^3y)\left[ \begin{matrix} r \\ 5 \end{matrix} \right] - \dots \\ &+ (-1)^r a^r (1+y, 1+a^{r-1}y) \equiv (-1)^r \{(1+ay)(1+a^2y)\dots(1+a^r y)\} \end{aligned} \quad (5)$$

where  $(1+y, 1+a^r y)$  denotes the product  $\{(1+y)(1+ay)\dots(1+a^r y)\}$  and  $\left[ \begin{matrix} r \\ p \end{matrix} \right]$  denotes  $\{(a^r-1)(a^{r-1}-1)\dots(a^p-1)\}$ .

This identity may be proved by substituting  $ay$  for  $y$  and  $-a$  for  $\delta$  in (1).

*Ex. 2.<sup>1</sup>*

$$\begin{aligned} &\{(1+a^{3^{r-1}}y)(1+a^{3^{r-1}+1}y)\dots(1+a^{3^r-3}y)\} \\ &\equiv {}^{3^r}S_{3^r} \{(1+y)(1+a^2y)(1+a^4y)\dots(1+a^{3^r-2}y)\} \\ &- {}^{3^r}S_{3^r-3} (a-1)\{(1+a^2y)(1+a^4y)\dots(1+a^{3^r-2}y)\} \\ &+ {}^{3^r}S_{3^r-6} (a^3-1)(a-1)\{(1+a^2y)(1+a^6y)\dots(1+a^{3^r-2}y)\} - \dots \\ &+ (-1)^k \{(a^{3^{k-1}}-1)(a^{3^k-3}-1)\dots(a-1)\} \\ &\times {}^{3^r}S_{3^r-3k} \{(1+a^{3^k}y)(1+a^{3^{k+1}}y)\dots(1+a^{3^r-2}y)\} + \dots \\ &+ (-1)^r \{(a^{3^{r-1}}-1)(a^{3^r-3}-1)\dots(a-1)\}. \end{aligned} \quad \dots (6)$$

<sup>1</sup> cf. "On the Evaluation of Some Factorable Continuants," Art 2, *Bul. Cal. Math. Soc.*, Vol. XIII. In subsequent references this paper will be called Paper 2.

*Proof.* The  $k+1$ th term in the right-hand-side expression of (1) is

$$= \{(1+a^{k-1}\delta)(1+a^{k-2}\delta)\dots(1+\delta)\} \frac{\{(a^r-1)(a^{r-1}-1)\dots(a^{k+1}-1)\}}{\{(a^{r-k}-1)(a^{r-k-1}-1)\dots(a-1)\}} \\ \times \{(y-\delta)(ay-\delta)\dots(a^{r-k-1}y-\delta)\}, \text{ by Art 6, Paper 3.}$$

Put

$$a = \frac{1}{b^s}, \quad y = b^{4r-3}z \quad \text{and} \quad \delta = -b^{2r-1} \quad \text{and let } {}^nB_r \text{ denote the sum of}$$

the products of  $n$  factors  $1, b, b^2, \dots, b^{n-1}$  taken  $r$  of them at a time. Then the  $k+1$ th term becomes

$$(-1)^k \{(b^{2k-1}-1)(b^{2k-3}-1)\dots(b^3-1)(b-1)\} \\ \times \frac{\{(b^{2r}-1)(b^{2r-1}-1)\dots(b^{2r-2k+1}-1)\}}{\{(b^{2k}-1)(b^{2k-1}-1)\dots(b^2-1)(b-1)\}} \\ \times {}^{2r-2k}B_{2r-2k} \{(1+b^{2k}z)(1+b^{2k+2}z)\dots(1+b^{2r-2}z)\} \\ = (-1)^k \{(b^{2k-1}-1)(b^{2k-3}-1)\dots(b^3-1)(b-1)\} \\ \times {}^{2r}B_{2r-2k} \{(1+b^{2k}z)(1+b^{2k+2}z)\dots(1+b^{2r-2}z)\}, \text{ by Art 6, Paper 3}$$

Hence the identity is proved.

*Ex. 3.*<sup>1</sup>

$$(1+a^{2r-1}y)(1+a^{2r-3}y)\dots(1+a^{2r-5}y) \\ \equiv {}^{2r-1}S_{2r-1} \{(1+y)(1+a^2y)\dots(1+a^{2r-4}y)\} \\ - {}^{2r-1}S_{2r-3}(a-1)\{(1+a^2y)(1+a^4y)\dots(1+a^{2r-4}y)\} + \dots \\ + (-1)^k {}^{2r-1}S_{2r-2k-1} \{(a^{2k-1}-1)(a^{2k-3}-1)\dots(a-1)\} \\ \times \{(1+a^{2k}y)(1+a^{2k+2}y)\dots(1+a^{2r-2}y)\} + \dots \\ + (-1)^{r-1} {}^{2r-1}S_1 \{(a^{2r-3}-1)(a^{2r-5}-1)\dots(a-1)\} \quad \dots \quad (7)$$

This may be proved in the same manner as *Ex. 2* by putting

$$a = \frac{1}{b^s}, \quad y = b^{4r-3}z \quad \text{and} \quad \delta = -b^{2r-1} \quad \text{in (1).}$$

<sup>1</sup> cf. Art 3, Paper 2.

2.<sup>1</sup>

$$\left[ \begin{smallmatrix} n \\ 1 \end{smallmatrix} \right] - \left[ \begin{smallmatrix} n-1 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 1 \\ 1 \end{smallmatrix} \right] + \left[ \begin{smallmatrix} n-2 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 2 \\ 1 \end{smallmatrix} \right] \cdot \frac{1+ay}{1+y} - \dots$$

$$\equiv 0 \text{ or } (-1)^{\frac{n}{2}} \left[ \begin{smallmatrix} n \\ 1 \end{smallmatrix} \right] \frac{\{(a-1)(a^3-1)\dots(a^{n-1}-1)\}}{\{(1+y)(1+a^2y)\dots(1+a^{n-2}y)\}}$$

according as  $n$  is odd or even; the last term of the series is

$$(-1)^n \left[ \begin{smallmatrix} n \\ 1 \end{smallmatrix} \right] \frac{\{(1+a^ny)(1+a^{n+2}y)\dots(1+a^{2n-3}y)\}}{\{(1+y)(1+a^2y)\dots(1+a^{n-2}y)\}}$$

$$\text{or } (-1)^n \left[ \begin{smallmatrix} n \\ 1 \end{smallmatrix} \right] \frac{\{(1+a^{n-1}y)(1+a^{n+1}y)\dots(1+a^{2n-3}y)\}}{\{(1+y)(1+a^2y)\dots(1+a^{n-2}y)\}} \quad \dots \quad (8)$$

according as  $n$  is odd or even.

*Proof.* Let  ${}^n\beta_r$  denote the series

$$\frac{{}^nS_r}{{}^rS_r} - \frac{{}^nS_{r+1}}{{}^{r+1}S_{r+1}} \frac{{}^{r+1}S_1}{{}^rS_r} + \frac{{}^nS_{r+2}}{{}^{r+2}S_{r+2}} \frac{{}^{r+2}S_2}{{}^rS_r} - \dots$$

$$+ (-1)^k \frac{{}^nS_{r+k}}{{}^{r+k}S_{r+k}} \frac{{}^{r+k}S_k}{{}^rS_r} + \dots + (-1)^{n-r} \frac{{}^nS_n}{{}^nS_n} \frac{{}^nS_{n-r}}{{}^rS_r}.$$

Since it can be shown, by Art 6, Paper 3, that

$$\frac{{}^nS_{r+k}}{{}^{r+k}S_{r+k}} \frac{{}^{r+k}S_k}{{}^rS_r} = \frac{{}^nS_r}{{}^rS_r} \cdot {}^{n-r}S_k.$$

we have

$${}^n\beta_r = \frac{{}^nS_r}{{}^rS_r} \{1 - {}^{n-r}S_1 + {}^{n-r}S_2 - \dots + (-1)^{n-r} {}^{n-r}S_{n-r}\} = 0, \text{ by (3)}$$

$$\therefore {}^n\beta_0 = {}^n\beta_1 = \dots = {}^n\beta_{n-1} = 0, \text{ but } {}^n\beta_n = \frac{{}^nS_n}{{}^nS_n} = 1. \quad \dots \quad (9)$$

<sup>1</sup> cf. Art 4, Paper 2.

<sup>2</sup> cf. Theorem (8), Paper 2.



Now let us take the particular case of (8) when  $n=7$ , an odd number, then the series is

$$\begin{aligned}
 & \left[ \begin{smallmatrix} 1 \\ 7 \\ 1 \end{smallmatrix} \right] - \left[ \begin{smallmatrix} 1 \\ 6 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 1 \\ 1 \end{smallmatrix} \right] + \left[ \begin{smallmatrix} 1 \\ 5 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 2 \\ 1 \end{smallmatrix} \right] \cdot \frac{1+ay}{1+y} \\
 & - \left[ \begin{smallmatrix} 1 \\ 4 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 3 \\ 1 \end{smallmatrix} \right] \cdot \frac{1+a^3y}{1+y} + \left[ \begin{smallmatrix} 1 \\ 3 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 4 \\ 1 \end{smallmatrix} \right] \cdot \frac{(1+a^3y)(1+a^5y)}{(1+y)(1+a^3y)} \\
 & - \left[ \begin{smallmatrix} 1 \\ 2 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 5 \\ 1 \end{smallmatrix} \right] \cdot \frac{(1+a^3y)(1+a^7y)}{(1+y)(1+a^3y)} \\
 & + \left[ \begin{smallmatrix} 1 \\ 1 \\ 1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} 6 \\ 1 \end{smallmatrix} \right] \cdot \frac{(1+a^3y)(1+a^7y)(1+a^9y)}{(1+y)(1+a^3y)(1+a^5y)} \\
 & - \left[ \begin{smallmatrix} 1 \\ 7 \\ 1 \end{smallmatrix} \right] \cdot \frac{(1+a^7y)(1+a^9y)(1+a^{11}y)}{(1+y)(1+a^3y)(1+a^5y)}.
 \end{aligned}$$

If we take the denominator of the last term as the common denominator, then the numerator becomes,

$$\begin{aligned}
 & (1+y)(1+a^3y)(1+a^5y) - {}^7S_1 (1+y)(1+a^3y)(1+a^5y) \\
 & + {}^7S_2 (1+ay)(1+a^3y)(1+a^5y) - \dots \\
 & + {}^7S_6 (1+a^3y)(1+a^7y)(1+a^9y) - {}^7S_7 (1+a^7y)(1+a^9y)(1+a^{11}y).
 \end{aligned}$$

If  $u_1 = (1+y)(1+a^3y)(1+a^5y)$ ,  $u_2 = (1+a^3y)(1+a^5y)$ , and  $u_3 = 1+a^3y$  then applying (6) to odd terms and (7) to even terms, we can show that the numerator

$$\begin{aligned}
 & = {}^7\beta_0 u_1 - {}^7\beta_2 u_2 (a-1) + {}^7\beta_4 u_3 (a^3-1)(a-1) \\
 & \quad - {}^7\beta_6 (a^6-1)(a^3-1)(a-1) = 0, \text{ by (9).}
 \end{aligned}$$

Thus the series vanishes.

If  $n=6$  an even number, we can similarly show that the numerator is

$${}^6\beta_0 u_1 - {}^6\beta_2 u_2 (a-1) + {}^6\beta_4 u_3 (a^3-1)(a-1) - (a^5-1)(a-1)(a^3-1)(a-1)(a-1).$$

$$\therefore \text{The series} = - \frac{(a^5-1)(a^3-1)(a-1)}{\left[ \begin{smallmatrix} 6 \\ 1 \end{smallmatrix} \right] (1+y)(1+a^2y)(1+a^4y)}.$$

The general case may be similarly treated.

### 3. The continuant

$$x - \frac{a^{n+1}-1}{a^3-1}, \quad -1.$$

$$\frac{(a^{n+1}-1)(a^{n-1}-1)a^2}{(a^5-1)(a-1)(1+a)^2}, x - \frac{(a^4+1)a}{(1+a)(1+a^2)}, \quad -1.$$

$$\frac{(a^{n+3}-1)(a^{n-3}-1)a^5}{(a^5-1)(a^3-1)(1+a^2)^2}, \quad x - \frac{(a^4+1)a^3}{(1+a^2)(1+a^3)}, \quad -1.$$

...

...

...

$$\frac{(a^{n+1}-1)(a-1)a^{n-4}}{(a^{n+1}-1)(a^{n-3}-1)(1+a^{n-1})^2}, \quad x - \frac{(a^4+1)a^{n-1}}{(1+a^{n-1})(1+a^n)}, \quad n$$

$$\equiv \{(x-1)(x-a^3)\dots(x-a)(x-a^{n-1})\}$$

... (10)

*Proof.* In evaluating this continuant we are to apply two algebraic relations viz.,

$$\frac{(a^{n+r}-1)}{(a^{s+r+1}-1)(1+a^r)} + \frac{(a^n+1)a^r}{(1+a^r)(1+a^{r+1})} - \frac{(a^{n-r-1}-1)a^{s+r+2}}{(a^{s+r+1}-1)(1+a^{r+1})} \equiv 1 \quad \dots (11)$$

$$\begin{aligned} \text{and } & \frac{(a^{n+r-k+2}-1)(a^{n+r-k+1}-1)(a^{n-r}-1)}{(a^{s+r+1}-1)(1+a^r)(a^{k-1}-1)} \\ & + \frac{(a^{n-r-k+1}-1)(a^{n+r-k+2}-1)(a^n+1)a^r}{(a^{k-1}-1)(1+a^r)(1+a^{r+1})} \\ & - \frac{(a^{n-r-k+1}-1)(a^{n-r-k}-1)(a^{n+r+1}-1)a^{s+1+2}}{(a^{s+r+1}-1)(1+a^{r+1})(a^{k-1}-1)} \\ & - (a^{n-k+1}-1) \equiv \frac{a^{k-1}(a^{n-r-k+1}-1)(a^{n+r-k+2}-1)}{(a^{k-1}-1)} \quad \dots (12) \end{aligned}$$

In the case of (12), if  $(1+a^r)(1+a^{r+1})(a^{s+r+1}-1)(a^{k-1}-1)$  be taken as the common denominator of the left-hand-side expression and the factors in each term of the numerator be multiplied together, the numerator will contain eighty terms of which sixty will be cancelled and the remaining twenty are :—

$$\begin{aligned} & -a^{2n-k+2} -a^{2n+r-k+2} -a^{2n+r-k+2} +a^{n-r} +a^{n+1} +a^{2n+2r-k+2} \\ & +a^{2n+2r-k+2} +a^{2n+2r-k+2} -a^{n+2r+2} -a^{n+2r+2} -a^{n+2r+2} \\ & -a^{n+2r+2} +a^n +a^{n+r+1} +a^{2r+k+1} +a^{2r+k} +a^{2r+k+1} \\ & -a^{k-1} -a^{r+k} -a^{r+k-1} \\ & =a^{k-1}(1+a^r)(1+a^{r+1})(a^{s+r+1}-1)(a^{n-r-k+1}-1)(a^{n+r-k+2}-1). \end{aligned}$$

Hence the theorem is proved. If we multiply both sides of (12) by  $a^{k-1}-1$  and then put  $k=1$ , we get the theorem (11).

Now let us consider the particular case of the continuant when  $n=4$  viz.,

$$\begin{array}{c}
 x - \frac{a^5-1}{a^3-1}, \quad -1 \\
 \hline
 \frac{(a^5-1)(a^3-1)a^3}{(a^3-1)(a-1)(1+a)^2}, \quad x - \frac{(a^4+1)a}{(1+a)(1+a^2)}, \quad -1, \\
 \hline
 \frac{(a^6-1)(a^3-1)a^5}{(a^3-1)(a^2-1)(1+a^2)^2}, \quad x - \frac{(a^4+1)a^3}{(1+a^2)(1+a^3)}, \quad -1 \\
 \hline
 \frac{(a^7-1)(a-1)a^5}{(a^7-1)(a^5-1)(1+a^3)^2}, \quad x - \frac{(a^4+1)a^3}{(1+a^2)(1+a^4)}
 \end{array}$$

On this perform the operations :—

$$\begin{aligned}
 & - \frac{(a^5-1)(a^3-1)(a-1)a^{15}}{(a^5-1)(a^3-1)(a-1)(1+a^3)(1+a^3)} \text{ col}_4 + \frac{(a^3-1)(a^2-1)a^7}{(a^3-1)(a-1)(1+a^2)} \text{ col}_3 - \frac{(a^3-1)a^3}{a-1} \text{ col}_2 + (a+1) \text{ col}_1 = \text{col}_4^{(1)}; \\
 & \frac{1}{x-a} \text{ col}_4^{(1)} + \frac{(a^3-1)(a-1)(a^6-1)a^7}{(a^3-1)(a-1)(1+a^3)(a-1)} \text{ col}_3 - \frac{(a^3-1)(a^5-1)a^3}{(a-1)^2} \text{ col}_2 + \frac{(a+1)(a^4-1)}{a-1} \text{ col}_1 = \text{col}_4^{(2)}; \\
 & \frac{1}{x-a} \text{ col}_4^{(2)} + 0 \text{ col}_3 - \frac{(a-1)(a^6-1)(a^4-1)a^3}{(a-1)^2(a^3-1)} \text{ col}_2 + \frac{(a^4-1)(a^3-1)}{(a-1)^2} \text{ col}_1 = \text{col}_4^{(3)}; \\
 & \frac{1}{x-a^2} \text{ col}_4^{(3)} + 0 \text{ col}_3 + 0 \text{ col}_2 + \frac{(a^4-1)(a^3-1)(a^3-1)}{(a-1)^2(a^3-1)} \text{ col}_1 = \text{col}_4^{(4)}.
 \end{aligned}$$

Then we shall find that all the elements, except the first, of the last column, vanish and hence the continuant is evaluated. Further when the elements of the last column, that result from any of these operations,  $k$ th for instance, are obtained in the simplest forms by the use of (11) and (12), they will contain  $x - a^{k-1}$  as a common factor while the other factors will be the multipliers themselves, the multiplier of  $r$ th column occurring in  $r$ th element. As an exception to this rule the last element of the last column is always zero except in the case of the first operation.

In the general case if  $m_r$  denote the multiplier of  $r$ th column and  $l$  that of the last column, we have

In the first operation

$$m_r = \lambda_r \begin{bmatrix} n-1 \\ n-r+1 \end{bmatrix}$$

where

$$\lambda_r = (-1)^{r-1} \frac{(a+1)a^{\frac{1}{2}(r-1)(3r-2)}}{\{(a^{2r-3}-1)(a^{2r-5}-1) \dots (a-1)\} \{(1+a)(1+a^3) \dots (1+a^{r-1})\}}$$

and  $l$  is governed by the same rule.

In the second operation

$$m_r = \lambda_r \begin{bmatrix} n-2 \\ n-r \end{bmatrix} \frac{a^{n+r-1}-1}{a-1} \quad \text{and} \quad l = \frac{1}{a-1}$$

and so on.

In the  $k$ th operation

$$m_r = \lambda_r \begin{bmatrix} n-k \\ n-r-k+2 \end{bmatrix} \begin{bmatrix} n+r-1 \\ n+r-k+1 \end{bmatrix} \bigg/ \begin{bmatrix} k-1 \\ 1 \end{bmatrix}$$

and

$$l = \frac{1}{x - a^{k-1}}.$$

4. (i).

$$\begin{aligned} & \begin{bmatrix} n-1 \\ n-r+1 \end{bmatrix} - \begin{bmatrix} n-2 \\ n-r \end{bmatrix}^{n+r-1} S_1 + \begin{bmatrix} n-3 \\ n-r-1 \end{bmatrix}^{n+r-1} S_2 - \dots \\ & + (-1)^{n-r} \begin{bmatrix} r-1 \\ 1 \end{bmatrix}^{n+r-1} S_{n-r} \end{aligned}$$

$$\equiv (-1)^{n-r} \begin{bmatrix} n-1 \\ n-r+1 \end{bmatrix} a^{\frac{1}{2}(n-r)(n+r-1)} \dots \quad (13)$$

*Proof.* Let us take the series

$$\left[ \begin{smallmatrix} n-1 \\ n-r+1 \end{smallmatrix} \right], \left[ \begin{smallmatrix} n-2 \\ n-r \end{smallmatrix} \right], \left[ \begin{smallmatrix} n-3 \\ n-r-1 \end{smallmatrix} \right] \dots \left[ \begin{smallmatrix} r-1 \\ 1 \end{smallmatrix} \right], 0, 0, 0, \dots$$

and obtain from it

$$\Delta_1, \Delta_2, \dots, \Delta_{r-1}, \Delta_r, \Delta_{r+1}, \dots, \Delta_n, \Delta_{n+1}, \dots, \Delta_{n+r-2}, \Delta_{n+r-1}$$

the successive orders of differences by using 1,  $a$ ,  $a^2$  etc., as the multipliers (see Art 5, Paper 3). Then the first term of  $\Delta_{n+r-1}$  is

$$(-1)^{n-r} a^{\frac{1}{2}(n-r)(n+r-1)} \left[ \begin{smallmatrix} n-1 \\ n-r+1 \end{smallmatrix} \right].$$

Hence the identity is proved by Art 5(i), Paper 3.

$$\begin{aligned} (ii) \quad & \frac{(a^p-1)a^{n-p}}{a^{n-p+1}-1} + \frac{a^{n+1}-1}{a^2-1} + \frac{(a^{n+1}-1)(a^{n-p-1}-1)a}{(a^{n-p+1}-1)(a^2-1)} \\ & = \frac{a^n-1}{a-1} \quad \dots \quad (14) \end{aligned}$$

and

$$\begin{aligned} & \frac{(a^{n-r}-1)(a^{n+r-p+1}-1)(a^{n+r-p}-1)}{(a^{n+1}-1)(a^r+1)(a^p-1)} - (a^{n-p}-1)a^{n-p-r} \\ & - \frac{(a^n+1)(a^{n+r-p+1}-1)(a^{n-p-r}-1)}{(1+a^r)(1+a^{r+1})(a^p-1)} \\ & - \frac{(a^{n+r+1}-1)(a^{n-p-r}-1)(a^{n-p-r-1}-1)a^{r+1}}{(a^{n+1}-1)(a^{r+1}+1)(a^p-1)} \equiv 0 \quad \dots \quad (15) \end{aligned}$$

These two theorems may be proved in the same manner as the theorem (12). From (15) it is clear that if in the left-hand-side expression of (12),  $(-1)$  be substituted for  $a^r$  in the second term,  $a^{r+1}$  for  $a^{n-r+2}$  in the third term and the fourth term be multiplied by  $a^{n-r-1+1}$ , the expression vanishes,



Thus in  $m_r$ , the highest power of  $x$  is  $n-r$  and the co-efficient of  $x^r$

$$\begin{aligned}
 &= \lambda_r \left\{ \left[ \begin{matrix} n-p-1 \\ n-r-p+1 \end{matrix} \right]^{n+r-1} S_p / {}^p S_p \right. \\
 &\quad - \left[ \begin{matrix} n-p-2 \\ n-r-p \end{matrix} \right]^{n+r-1} S_{p+1} {}^{p+1} S_1 / {}^{p+1} S_{p+1} \\
 &\quad + \left[ \begin{matrix} n-p-3 \\ n-r-p-1 \end{matrix} \right]^{n+r-1} S_{p+2} {}^{p+2} S_2 / {}^{p+2} S_{p+2} - \dots \\
 &\quad \left. + (-1)^{n-r-p} \left[ \begin{matrix} r-1 \\ 1 \end{matrix} \right]^{n+r-1} S_{n-r} {}^{n-r} S_{n-r-p} / {}^{n-r} S_{n-r} \right\} \\
 &= \lambda_r \frac{{}^{n+r-1} S_p}{{}^p S_p} \left\{ \left[ \begin{matrix} n-p-1 \\ n-r-p+1 \end{matrix} \right] - \left[ \begin{matrix} n-p-2 \\ n-r-p \end{matrix} \right] {}^{n+r-p-1} S_1 \right. \\
 &\quad + \left[ \begin{matrix} n-p-3 \\ n-r-p-1 \end{matrix} \right] {}^{n+r-p-1} S_2 - \dots \\
 &\quad \left. + (-1)^{n-r-p} \left[ \begin{matrix} r-1 \\ 1 \end{matrix} \right] {}^{n+r-p-1} S_{n-r-p} \right\} \\
 &= \lambda_r \frac{{}^{n+r-1} S_p}{{}^p S_p} (-1)^{n-p-r} \left[ \begin{matrix} n-p-1 \\ n-p-r+1 \end{matrix} \right] a^{\frac{1}{2}(n-p-r)(n-p+r-1)} \text{ by (13)}
 \end{aligned}$$

Substituting the value of  $\lambda_r$ , we have the co-efficient of  $x^r$

$$\begin{aligned}
 &= (-1)^{n-p-1} \frac{\left[ \begin{matrix} n+r-1 \\ n+r-p \end{matrix} \right]}{\left[ \begin{matrix} p \\ 1 \end{matrix} \right]} \left[ \begin{matrix} n-p-1 \\ n-p-r+1 \end{matrix} \right] a^{\frac{1}{2}(n-p)(n-p-1)+(r-1)^2} \\
 &\quad \times \frac{(a+1)\{(a-1)(a^2-1)\dots(a^{r-1}-1)\}}{\{(a^{2r-2}-1)(a^{2r-3}-1)\dots(a^2-1)(a-1)\}} \\
 &= (-1)^{n-p-1} \frac{{}^{n+r-1} S_p {}^{n-p-1} S_{r-1} (a+1)}{{}^{n-p-1} S_{r-1}} a^{\frac{1}{2}(n-2p)(n-1)+(r-1)^2}
 \end{aligned}$$

Since  $n$  is the order of the continuant, we may divide each multiplier by

$$(-1)^{n-1} (a+1) a^{\frac{1}{2}n(n-1)}$$



and take the coefficient of  $x^p$  in  $m_r$  as

$$\begin{aligned}
 & (-1)^p \frac{a^{n+r-1} S_p^{n-p-1} S_{r-1}}{a^{r-2} S_{r-1}} \cdot \frac{a^{(r-1)^2}}{a^{p(n-1)}} \\
 \therefore m_r = & \frac{a^{(r-1)^2}}{a^{r-2} S_{r-1}} \left\{ a^{n-1} S_{r-1} - \frac{1}{a^{n-1}} a^{n-2} S_{r-1} a^{n+r-1} S_1 a \right. \\
 & + \frac{1}{a^{2(n-1)}} a^{n-2} S_{r-1} a^{n+r-1} S_2 a^2 - \dots \\
 & + (-1)^{n-r-1} \frac{1}{a^{(n-r-1)(n-1)}} a^{r-1} S_{r-1} a^{n+r-1} S_{n-r-1} a^{n-r-1} \\
 & \left. + (-1)^{n-r} \frac{1}{a^{(n-r)(n-1)}} a^{r-1} S_{r-1} a^{n+r-1} S_{n-r} a^{n-r} \right\} \dots \quad (16)
 \end{aligned}$$

The multiplier of the last column

$$= \left[ \begin{smallmatrix} n-1 \\ 1 \end{smallmatrix} \right] \lambda_n \div (-1)^{n-1} (a+1) a^{\frac{1}{2}n(n-1)} = \frac{a^{(n-1)^2} a^{n-1} S_{n-1}}{a^{n-2} S_{n-1}} \quad (17)$$

Thus this multiplier may also be obtained by (16).

(i) Now if the single operation obtained by means of the formula (16) be performed on the continuant of the  $n$ th order, then from the first row we have

$$\left( x - \frac{a^{n+1}-1}{a^2-1} \right) m_1 - m_2,$$

in which the coefficient of  $x^p$

$$\begin{aligned}
 & = (-1)^{p-1} \frac{1}{a^{p(n-1)}} \left\{ a^{n-1} S_{p-1} a^{n-1} + \frac{a^{n+1}-1}{a^2-1} a^{n-2} S_p + \frac{a^{n+1} S_p^{n-p-1} S_1 a}{a^2 S_1} \right\} \\
 & = (-1)^{p-1} a^{\frac{1}{2}p(p-2n+1)} \frac{\left[ \begin{smallmatrix} n \\ n-p+1 \end{smallmatrix} \right]}{\left[ \begin{smallmatrix} p \\ 1 \end{smallmatrix} \right]} \frac{a^n-1}{a-1} \text{ by (14)} \\
 & = (-1)^{p-1} \frac{1}{a^{\frac{1}{2}n(n-1)}} \cdot \frac{a^n-1}{a-1} a^{n-p}.
 \end{aligned}$$

$$\begin{aligned}
& \therefore \left( x - \frac{a^{n+1}-1}{a^2-1} \right) m_1 - m_2 \\
& = (-1)^{n-1} \frac{1}{a^{\frac{1}{2}n(n-1)}} \frac{a^n-1}{a-1} \{ x^n - {}^nS_1 x^{n-1} + {}^nS_2 x^{n-2} - \dots + (-1)^n {}^nS_n \} \\
& = (-1)^{n-1} \frac{1}{a^{\frac{1}{2}n(n-1)}} \cdot \frac{a^n-1}{a-1} \{ (x^n-1)(x-a)\dots(x-a^{n-1}) \} \quad \dots \quad (18)
\end{aligned}$$

which is the first element of the last column:

From the  $r+1$ th row, we get

$$\begin{aligned}
& \frac{(a^{n+r}-1)(a^{n-1}-1)a^{s_{r-1}}}{(a^{s_{r+1}}-1)(a^{s_{r-1}}-1)(1+a^r)^2} m_r \\
& + \left\{ x - \frac{(a^n+1)a^r}{(1+a^r)(1+a^{r+1})} \right\} m_{r+1} - m_{r+2}
\end{aligned}$$

in which the coefficient of  $x^n$  is

$$\begin{aligned}
& = (-1)^n \frac{\left[ \begin{smallmatrix} n+r \\ n+r-p+2 \end{smallmatrix} \right] \left[ \begin{smallmatrix} n-p-1 \\ n-p-r+1 \end{smallmatrix} \right] a^{s_{r-1}} a^{(r-1)^2} {}^rS_r}{\left[ \begin{smallmatrix} 2r \\ r+1 \end{smallmatrix} \right] \left[ \begin{smallmatrix} p-1 \\ 1 \end{smallmatrix} \right] a^{p(n-1)}} \\
& \times \left\{ \frac{(a^{n-r}-1)(a^{n+r-p+1}-1)(a^{n+r-p}-1)}{(a^{s_{r+1}}-1)(1+a^r)(a^p-1)} - (a^{n-p}-1)a^{n-p-r} \right. \\
& - \frac{(a^n+1)(a^{n+r-p+1}-1)(a^{n-p-r}-1)}{(1+a^r)(1+a^{r+1})(a^p-1)} \\
& \left. - \frac{(a^{n+r+1}-1)(a^{n-p-r-1}-1)(a^{n-p-r}-1)a^{r+1}}{(a^{s_{r+1}}-1)(1+a^{r+1})(a^p-1)} \right\} = 0, \text{ by (15)}
\end{aligned}$$

Thus  $(r+1)$ th element of the last column is zero. Similarly all the elements, except the first, of the last column vanish.

The product of the elements of the lower minor diagonal

$$= \frac{\left[ \begin{smallmatrix} n-1 \\ 1 \end{smallmatrix} \right]^2 (a-1) a^{2(n-1)^2}}{\left[ \begin{smallmatrix} 2n-2 \\ 1 \end{smallmatrix} \right] (a^n-1)^{n-1} S_{n-1}} = \frac{(a-1) a^{2(n-1)^2}}{{}^{2n-2}S_{n-1} (a^n-1)} \quad \dots \quad (19)$$

Hence the value of the continuant follows readily from (17), (18) and (19).

(ii) To illustrate the application of the formula (16), let us consider the continuant of the 5th order, then the single operation is

$$\begin{aligned} & \frac{a^{16}}{S_4} \cdot S_4 \text{col}_5 + \frac{a^9}{S_5} \left\{ S_5 - \frac{1}{a^4} S_5^6 S_1 x \right\} \text{col}_4 + \frac{a^4}{S_2} \left\{ S_2 - \frac{1}{a^4} S_2^7 S_1 x + \frac{1}{a^8} S_2^7 S_2^7 S_2^7 \right\} \text{col}_1, \\ & + \frac{a}{S_1} \left\{ S_1 - \frac{1}{a^4} S_1^6 S_1 x + \frac{1}{a^8} S_1^6 S_2 x^2 - \frac{1}{a^{12}} S_1^6 S_3 x^3 \right\} \text{col}_2 + \left\{ 1 - \frac{1}{a^4} S_1 x + \frac{1}{a^8} S_2 x^2 - \frac{1}{a^{12}} S_3 x^3 + \frac{1}{a^{16}} S_4 x^4 \right\} \text{col}_1. \end{aligned}$$

On performing this operation we have the continuant

$$\begin{array}{c|c|c|c} = \frac{S_4}{S_4 a^{16}} x - \frac{a^6 - 1}{a^3 - 1}, & -1, & 0, & 0, \frac{1}{a^{10}} \cdot \frac{a^5 - 1}{a - 1} \{ (x - 1)(x - a) \dots (x - a^4) \} \\ \hline & \frac{(a^6 - 1)(a^4 - 1)a^2}{(a^3 - 1)(a - 1)(1 + a)^2}, x - \frac{(a^6 + 1)a}{(1 + a)(1 + a^2)}, & -1, & 0 \\ \hline & \frac{(a^7 - 1)(a^3 - 1)a^5}{(a^2 - 1)(a^3 - 1)(1 + a^2)^2}, x - \frac{(a^5 + 1)a^2}{(1 + a^2)(1 + a^3)}, & -1, & 0 \\ \hline & \frac{(a^8 - 1)(a^2 - 1)a^8}{a^7 - 1)(a^5 - 1)(1 + a^2)^2}, x - \frac{(a^5 + 1)a^3}{(1 + a^2)(1 + a^4)}, & & 0 \\ \hline & \frac{(a^9 - 1)(a - 1)a^{11}}{(a^2 - 1)(a^7 - 1)(1 + a^4)^2}, & & 0 \end{array}$$

$$= (x - 1)(x - a)(x - a^2)(x - a^3)(x - a^4).$$

Here the elements of the last column may be obtained by the theorems (14) and (15), taking  $r$  equal to 1 less than the number of the row which is considered.

Ex. 1. Since

$$\frac{a^r - 1}{a^p - 1} = \frac{1 + a + a^2 + \dots + a^{r-1}}{1 + a + a^2 + \dots + a^{p-1}} = \frac{r}{p} \text{ if } a=1$$

$\therefore$  as a particular case of the continuant of Art 3 when  $a=1$ , we have

$$\left| \begin{array}{cccc} x - \frac{n+1}{2}, & -1, & & \\ \frac{(n+1)(n-1)}{3 \cdot 1 \cdot 2^2}, & x - \frac{1}{2}, & -1, & \\ & \frac{(n+2)(n-2)}{5 \cdot 3 \cdot 2^3}, & x - \frac{1}{2}, & -1, \\ & \dots & \dots & \dots \\ & & & \frac{(2n-1) \cdot 1}{(2n-1)(2n-3)2^n}, x - \frac{1}{2} \end{array} \right|_n$$

$$= (r-1)^n.$$

6. In the language of Mr. Datta<sup>1</sup> the Heilermann's Theorem is :—  
If the series

$$\frac{a_0}{a^p} + \frac{a_1}{a^{\frac{p}{2}}} + \frac{a_2}{a^{\frac{p}{3}}} + \dots \quad \dots \quad (20)$$

is converted into a continued fraction of the form

$$\frac{a_1}{x+b_1} + \frac{a_2}{x+b_2} + \frac{a_3}{x+b_3} + \dots \quad \dots \quad (21)$$

then the elements of the continued fraction are given by

$$a_r = \frac{k_{r-2} k_r}{k_{r-1}^2} \text{ and } b_r = \frac{1}{k_{r-1}} \frac{k_{r-1}}{k_r} - \frac{1}{k_r}.$$

where  $k_{r+1} = \left| \begin{array}{ccccc} a_r, & a_{r-1}, & \dots & a_1, & a_0 \\ a_{r+1}, & a_r, & \dots & a_2, & a_1 \\ \dots & \dots & \dots & \dots & \dots \\ a_{2r}, & a_{2r-1}, & \dots & a_{r+1}, & a_r \end{array} \right|$

and  ${}^p k_r$  is obtained from  $k_{r+1}$  by deleting the  $p+1$ th column and the last row. Moreover if  $f_r(x)$  and  $\phi_{r-1}(r)$  are respectively the

<sup>1</sup> Haripada Datta. "On the Failure of Heilermann's Theorem." *Proc. Edin. Math. Soc.*, Vol. 35. 1916-1917.

denominator and the numerator of the  $r$ th convergent then

$$f_r(x) = x^r - \frac{{}^1k_r}{k_r} x^{r-1} + \frac{{}^2k_r}{k_r} x^{r-2} - \dots + (-1)^r \frac{{}^rk_r}{k_r}$$

and  $\phi_{r-1}(x) = \gamma_{r-1} x^{r-1} + \gamma_{r-2} x^{r-2} + \dots + \gamma_1 x + \gamma_0$

where  $\gamma_0 = a_{r-1} - \frac{{}^1k_r}{k_r} a_{r-2} + \frac{{}^2k_r}{k_r} a_{r-3} - \dots + (-1)^{r-1} \frac{{}^{r-1}k_r}{k_r} a_0$

$$\gamma_1 = a_{r-2} - \frac{{}^1k_r}{k_r} a_{r-3} + \dots + (-1)^{r-2} \frac{{}^{r-2}k_r}{k_r} a_0$$

$$\dots \dots \dots$$

$$\gamma_{r-2} = a_1 - \frac{{}^1k_r}{k_r} a_0 \qquad \gamma_{r-1} = a_0$$

The successive convergents to the continued fraction (21) have the property that if the  $n$ th convergent is expanded as a power-series in  $\frac{1}{x}$ , the first  $2n$  terms of this expansion will be, term for term, the same as the first  $2n$  terms of the series (20) " "

If, by the above theorem, the series

$$-\frac{{}^nS_1}{x} + \frac{{}^nS_2}{x^2} - \frac{{}^nS_3}{x^3} + \dots + (-1)^n \frac{{}^nS_n}{x^n} \dots \quad (23)$$

be converted into a continued fraction of the form (21), then the elements of the continued fraction will be given by

$$a_1 = \frac{a^n - 1}{1 - a}, \quad b_1 = -\frac{a^{n-1} - 1}{1 - a^n} a$$

$$a_r = \frac{(a^{n+r-1} - 1)(a^{n-r+1} - 1)a^{3r-4}}{(1 - a^{2r-1})(1 - a^{2r-3})(1 + a^{r-1})^2} \text{ and } b_r = -\frac{(a^n + 1)a^{r-1}}{(1 + a^{r-1})(1 + a^r)}$$

*Proof.* If we expand by division the first convergent  $\frac{a_1}{x + b_1}$  as a power series in  $\frac{1}{x}$  and equate the first two terms of this expansion with the first two terms of the series (23), we can readily get  $a_1$  and  $b_1$ . For other elements we are to find out  $k_r$  and  ${}^1k_r$ .

If  $s_r = (-1)^r {}^nS_r$  then

$$k_r = \begin{vmatrix} s_4 & s_3 & s_2 & s_1 \\ s_5 & s_4 & s_3 & s_2 \\ s_6 & s_5 & s_4 & s_3 \\ s_7 & s_6 & s_5 & s_4 \end{vmatrix}$$

\* For the other part of this theorem, see Datta's paper "On the Theory of Continued Fractions" *Proc. Edin. Math. Soc.*, Vol. 35, 1916-1917.

$$\begin{aligned}
 &= s_1 s_2 s_3 s_4 a^{10} \begin{vmatrix} \frac{(a^{n-1}-1)(a^{n-2}-1)(a^{n-3}-1)}{(1-a^2)(1-a^3)(1-a^4)}, & \frac{(a^{n-1}-1)(a^{n-2}-1)}{1-a^2}, & 1 \\ \frac{(a^{n-2}-1)(a^{n-3}-1)(a^{n-4}-1)}{(1-a^3)(1-a^4)(1-a^5)}, & \frac{a^{n-2}-1}{1-a^2} a, & 1 \\ \frac{(a^{n-3}-1)(a^{n-4}-1)(a^{n-5}-1)}{(1-a^4)(1-a^5)(1-a^6)}, & \frac{a^{n-3}-1}{1-a^2} a^2, & 1 \\ \frac{(a^{n-4}-1)(a^{n-5}-1)(a^{n-6}-1)}{(1-a^5)(1-a^6)(1-a^7)}, & \frac{a^{n-4}-1}{1-a^2} a^3, & 1 \end{vmatrix}
 \end{aligned}$$

On this determinant perform the operations row<sub>1</sub> ← row<sub>2</sub>; row<sub>2</sub> ← row<sub>3</sub> and row<sub>3</sub> ← row<sub>4</sub> and then by the algebraic relation

$$\frac{a^k-1}{1-a^i} - \frac{a^k-a^m}{1-a^{i+m}} = \frac{(a^{k+i}-1)(1-a^m)}{(1-a^i)(1-a^{i+m})} \quad \dots \quad (24)$$

$$\begin{aligned}
 \text{we have } k_4 = s_1 s_2 s_3 s_4 a^{13} & \begin{vmatrix} \frac{(a^{n+1}-1)^2(1-a^2)(1-a^3)(1-a^4)}{(1-a^2)(1-a^3)^2(1-a^4)^2(1-a^5)}, & \frac{a^{n-2}-1}{1-a^2}, & 1 \\ \frac{(a^{n-2}-1)(a^{n-3}-1)(a^{n-4}-1)}{(1-a^3)(1-a^4)(1-a^5)}, & \frac{a^{n-3}-1}{1-a^2} a, & 1 \\ \frac{(a^{n-3}-1)(a^{n-4}-1)(a^{n-5}-1)}{(1-a^4)(1-a^5)(1-a^6)}, & \frac{a^{n-4}-1}{1-a^2} a^2, & 1 \\ \frac{(a^{n-4}-1)(a^{n-5}-1)(a^{n-6}-1)}{(1-a^5)(1-a^6)(1-a^7)}, & \frac{a^{n-5}-1}{1-a^2} a^3, & 1 \end{vmatrix}
 \end{aligned}$$



# ON AN APPLICATION OF BESSEL FUNCTIONS TO PROBABILITY

By

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1. Some remarkable definite integrals involving Bessel Functions have been evaluated by Sonine in his elaborate memoir<sup>1</sup> in the *Math. Annalen*. Nicholson<sup>2</sup> in the *Quarterly Journal* generalised some of Sonine's results.

"A very remarkable advance in the theory of random variations and of flights in two dimensions is due to J. C. Kluyver<sup>3</sup> who has discovered an expression for the probability of various resultants in the form of a definite integral involving Bessel Functions. His exposition is rather concise." His paper has been reproduced with slight changes of notation by Lord Rayleigh<sup>4</sup> who has studied various aspects of the problem and also given the most general result of one of the particular cases.

In a previous paper,<sup>5</sup> I have attempted to evaluate more general forms of some of the integrals given by Sonine. In the first part of the present paper, I have employed the method used in my previous paper to extend the results obtained therein and have given a very general case of the integral involving the product of a number of Bessel Functions. In the second part, I have applied this general form to the problem studied by Kluyver and have obtained by a *completely different method* the result obtained therein.

I am indebted to Dr. S. K. Banerji for directing my attention to Kluyver's result and also to Rai A. C. Bose Bahadur for his valuable suggestions.

<sup>1</sup> Sonine, *Math. Annalen*, Band 16, page 1.

<sup>2</sup> Nicholson, *Quar. Journal*, Vol. 48, part IV (1920) p 321.

<sup>3</sup> J. C. Kluyver, *Koninklijke Akademie Van Wetenschappen te Amsterdam, Verslag van de gewone vergaderingen des Wisen-Naturkundige Afdeling*, Deel XIV, 1st Gedeelte, 30 Sept, 1905, pp. 305-24.

<sup>4</sup> Lord Rayleigh, *Scientific Papers*, Vol. VI, page 610.

<sup>5</sup> Datta, *Bull. Cal. Math. Soc.*, Vol. XI, No. 4, p. 221.



2. Sonine has given the elegant formula

$$\begin{aligned} & \int_0^{\infty} J_m(pr) J_m(qr) e^{-hr^2} r dr \\ &= \frac{p^m q^m}{\sqrt{\pi} 2^m \Gamma(m + \frac{1}{2})} \frac{1}{(2h)^{m+1}} \int_{-1}^1 e^{\frac{1-p^2+q^2-2pqt}{4h}} (1-t^2)^{m-\frac{1}{2}} dt \\ & \quad (m > -\frac{1}{2}). \quad \dots (1) \end{aligned}$$

It has been shown by me in my previous paper "On an Extension of Sonine's Integral in Bessel Functions" that by substituting, in the above, for  $h$ ,  $h + \frac{c}{2u}$  and multiplying both sides by  $\frac{1}{2\pi} e^{\frac{c^2}{2}} \frac{dr}{u^{m+1}}$  and integrating with respect to  $r$  between the limits  $-\infty$  and  $+\infty$ , we have

$$\begin{aligned} & \int_0^{\infty} J_m(pr) J_m(qr) J_m(cr) e^{-hr^2} r dr \\ &= \frac{p^m q^m c^m}{\sqrt{\pi} 2^{2m} \sqrt{\pi} \{\Gamma(m + \frac{1}{2})\}^2} \int_{-1}^1 (1-t^2)^{m-\frac{1}{2}} \frac{dt}{(2h)^{m+1}} \\ & \quad \times \int_{-1}^1 e^{\frac{1-c^2+v^2-2crz}{4h}} (1-z^2)^{m-\frac{1}{2}} dz \\ & \quad (m > -\frac{1}{2}) \quad (2) \end{aligned}$$

where  $v^2$  is equal to  $p^2 + q^2 - 2pqt$  and is a positive quantity.

The analogy between the two equations (1) and (2) suggests that we can employ the method indicated above to obtain the integral of the product of four Bessel Functions.

Thus, substituting for  $h$ ,  $h + \frac{b}{2u}$ , and repeating the same process, we can write

$$\begin{aligned} & \int_0^\infty J_m(px) J_m(qx) J_m(cx) J_m(bx) e^{-hx^2} \frac{dx}{x^{2m-1}} \\ &= \frac{p^m q^m c^m b^m}{\pi 2^{2m} \sqrt{\pi} \{\Gamma(m + \frac{1}{2})\}^2} \int_{-1}^1 (1-t^2)^{m-\frac{1}{2}} \frac{dt}{(2h)^{m+1}} \\ & \quad \times \int_{-1}^1 (1-z^2)^{m-\frac{1}{2}} dz \int_{-1}^1 e^{-\frac{b^2 + \omega^2 - 2b\omega y}{4h}} (1-y^2)^{m-\frac{1}{2}} dy \end{aligned}$$

where  $\omega^2 = c^2 + v^2 - 2cvz$  and  $m > -\frac{1}{2}$ .

Using the same method to obtain the integral of the product of any number of Bessel Functions, we can write as a general form (number of Bessel Functions being  $n$ )

$$\begin{aligned} & \int_0^\infty J_m(px) J_m(qx) J_m(cx) J_m(bx) \dots J_m(hx) e^{-hx^2} \frac{dx}{x^{m(n-2)+1}} \\ &= \frac{p^m q^m c^m b^m \dots h^m}{\{\pi\}^{\frac{n-1}{2}} \{\Gamma(m + \frac{1}{2})\}^{\frac{n-1}{2}} 2^{m(n-1)}} \int_{-1}^1 (1-t^2)^{m-\frac{1}{2}} dt \\ & \quad \times \int_{-1}^1 \dots \int_{-1}^1 \int_{-1}^1 e^{-\frac{k^2 + u^2 - 2uk\alpha}{4h}} (1-\alpha^2)^{m-\frac{1}{2}} d\alpha \\ & \quad [m > -\frac{1}{2}]. \end{aligned}$$

Now substituting for  $h$ ,  $h = \frac{l}{2u}$ , and multiplying both sides by

$$\frac{1}{2\pi} e^{\frac{lu}{2} - \frac{ly^2}{2u}} \frac{dr}{u^{\frac{n+1}{2}}}$$

and integrating with regard to  $r$  between the limits  $-\infty$  and  $+\infty$ , we have

$$\begin{aligned} & \int_0^\infty J_m(px) J_m(qx) J_m(cx) \dots J_m(kx) \frac{J_n(l\sqrt{x^2+\gamma^2}) dx}{x^{m(n-1)-1} (\sqrt{x^2+\gamma^2})^n} \\ &= \frac{p^m q^m c^m \dots k^m l^{-n}}{\{\pi\}^{\frac{n-1}{2}} \{\Gamma(m+\frac{1}{2})\}^{\frac{n-1}{2}} 2^{m(n-1)}} \int_{-1}^1 (1-t^2)^{m-\frac{1}{2}} dt \iint \dots \\ & \times \int_{\beta}^1 (1-a^2)^{m-\frac{1}{2}} J_{n-m-1}(\gamma\sqrt{l^2-k^2-u^2+2uka}) \\ & \times (\sqrt{l^2-k^2-u^2+2uka})^{n-m-1} \gamma^{m-n+1} da. \end{aligned}$$

where  $\beta=1$ , for  $l^2 < (k-u)^2$ ;

$$\beta = \frac{k^2+u^2-l^2}{2ku}, \text{ for } (k-u)^2 < l^2 < (k+u)^2;$$

$$\beta = -1, \text{ for } l^2 > (k+u)^2.$$

For  $\gamma=0$ , we obtain

$$\begin{aligned} & \int_0^\infty J_m(px) J_m(qx) \dots \frac{J_m(kx) J_n(lx)}{x^{m(n-1)+(n-1)}} dx \\ &= \frac{p^m q^m \dots k^m l^{-n}}{\{\sqrt{\pi}\}^{\frac{n-1}{2}} \{(m+\frac{1}{2})\}^{\frac{n-1}{2}} 2^{m(n-1)}} \int_{-1}^1 (1-t^2)^{m-\frac{1}{2}} dt \\ & \times \int_{-1}^1 \dots \int_{\beta}^1 (1-a^2)^{m-\frac{1}{2}} (\sqrt{l^2-k^2-u^2+2uka})^{n-m-1} da. \end{aligned}$$

$$n > m > -\frac{1}{2}.$$

Now if  $n=m+1$

$$\begin{aligned} & \int_0^1 J_m(px) J_m(qr) \dots J_m(kx) \frac{J_{m+1}(lx)}{x^{m^2+m}} dx \\ &= \frac{p^m q^m \dots k^m l^{-m-1}}{\{\sqrt{\pi}\}^{\frac{n-1}{2}} \{\Gamma(m+\frac{1}{2})\}^{\frac{n-1}{2}} 2^{mm}} \\ & \int_{-1}^1 (1-t^2)^{m-\frac{1}{2}} dt \dots \int_{\beta}^1 (1-a^2)^{m-\frac{1}{2}} da. \end{aligned}$$

Now if  $m=0$ ,

$$\begin{aligned} & \int_{-1}^1 J_0(px) J_0(qr) \dots J_0(kr) J_1(lx) dx \\ &= \frac{1}{l\pi^{n-1}} \int_{-1}^1 (1-t^2)^{-\frac{1}{2}} dt \dots \int_{\beta}^1 (1-a^2)^{m-\frac{1}{2}} da. \end{aligned}$$

If in this integral, we put

$$t = \cos \theta_1, \dots, a = \cos \theta_{n-1},$$

we get (the number of Bessel Functions being  $n+1$ )

$$\begin{aligned} & l \int_0^{\infty} J_0(px) J_0(qr) \dots J_0(kr) J_1(lr) dx \\ &= \left(\frac{2}{\pi}\right)^{n-1} \int_0^{\frac{\pi}{2}} d\theta_1 \dots \int_0^{\frac{\pi}{2}} d\theta_{n-1}. \quad \dots \quad (I) \end{aligned}$$

3. It would appear from the above that there are certain relations between  $p, q, c, \dots, k, l; v, \omega, \dots, u$  and  $t, z, \dots, a$ . These may be interpreted geometrically thus,

$$\text{Since } v^2 = p^2 + q^2 - 2pqt \quad \text{where } t = \cos \theta_1,$$

$$\omega^2 = c^2 + v^2 - 2cvz \quad ,, \quad z = \cos \theta_2,$$

$$\dots \quad \dots \quad \dots$$

$$l^2 = t^2 + u^2 - 2uka \quad ,, \quad a = \cos \theta_{n-1},$$

it is clear that  $t$  is the cosine of angle of the triangle having  $p, v$  and  $q$  for its sides included between the sides  $p$  and  $q$ ;  $z$  is the cosine of the angle of the triangle having  $c, v$  and  $b$  for its sides included between the sides  $c$  and  $v$  and so on. Hence it is obvious that  $p, q, c, \dots, k, l$  form a polygon having  $v, \omega, \dots, u$  as the successive diagonals joining one of the angular points to all others in succession. Hence it is evident from the above geometrical interpretation that the integral on the left hand side is equal to the multiple integral on the right hand side or zero according as

$$v^2 = p^2 + q^2 - 2pqt \text{ or not}$$

$$\omega^2 = c^2 + v^2 - 2cvz \text{ or not}$$

$$l^2 = k^2 + u^2 - 2uka \text{ or not}$$

i.e., according as we can form a triangle having  $p, q$ , and  $v$  for its sides or not, because only in the former case  $v$  is a real positive quantity; according as we can form a triangle having  $c, v$  and  $\omega$  as its sides or not, because the integral is not equal to zero when  $\omega$  is a real positive quantity and that is only possible when  $\omega$  is the third side of the triangle having  $c, \omega$ , and  $v$  for its sides; and so on; and hence (combining the above conditions) we see that according as we can form a polygon having  $p, q, c, \dots, k, l$  as its sides,  $v, \omega, \dots, u$  being the successive diagonals joining one of the vertices to all others.

4. "We are now in a position to investigate the probability  $P_n(r|l_1, l_2, \dots, l_n)$  that after  $n$  stretches  $l_1, l_2, \dots, l_n$  taken in directions at random, the distance from the stretching point  $O$  shall be less than an assigned magnitude  $r$ . The direction of the first stretch  $l$  is plainly a matter of indifference. On the other hand, the probability that the angles  $\theta$  lie within the limits  $\theta_1$  and  $\theta_1 + d\theta_1, \theta_2$  and  $\theta_2 + d\theta_2, \dots, \theta_{n-1}$  and  $\theta_{n-1} + d\theta_{n-1}$  is  $\frac{1}{(\pi)^{n-1}} d\theta_1 d\theta_2 \dots d\theta_{n-1}$  which is now to be integrated under the conditions that the  $n$ th radius vector shall be less than  $r$ ."

We have shown in the previous articles that

$$\int_0^{\infty} J_0(px) J_0(qx) \dots dx$$

$$= \left( \frac{2}{\pi} \right)^{n-1} \int_0^{\pi/2} d\theta_1 \int_0^{\pi/2} d\theta_2 \dots \int_0^{\pi/2} d\theta_n \text{ or zero}$$

according as we can form a polygon having  $p, q, \dots$  for its sides and  $v, \omega, \dots$  as its successive diagonals or not. Hence the probability that the  $(n+1)$ th radius vector after  $(n+1)$  stretches shall be less than an assigned magnitude is

$$P_r(p, q, \dots) = \int_0^{\infty} J_0(px) \dots dx$$

[number of Bessel functions being  $n+1$ ].

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# ON VORTEX RINGS OF FINITE CIRCULAR SECTION IN INCOMPRESSIBLE FLUIDS

By

NRIPENDRANATH SEN

## *Introduction.*

1. In a recent issue <sup>1</sup> of the *Bulletin of the Calcutta Mathematical Society*, it has been shewn that when the vorticity at any point of a moving circular vortex ring of finite section varies as the  $n^{\text{th}}$  power of the distance of the point from the axis of the ring, its cross-section does not remain circular but gets elongated in the direction of its motion of translation. Although the steady motion of vortex rings has attracted considerable attention of many eminent mathematicians including Kelvin <sup>2</sup>, Hicks <sup>3</sup>, Chree <sup>4</sup>, Basset <sup>5</sup>, Dyson <sup>6</sup>, Thomson <sup>7</sup> and others, no previous writer has attempted the problem of the motion of vortex rings of finite circular section.

In the present paper, I have shown that for a certain law of vorticity, it is possible for a ring to move with invariable circular section. The law of vorticity and the velocity of translation have been calculated for fairly thick rings. It has been found that to a certain approximation the velocity of translation is identical with that of a ring with constant vorticity, this being due to the fact that correct to that order of approximation the vorticity may be supposed to be constant over the cross section of the ring.

<sup>1</sup> Nripendranath Sen—"On Circular Vortex Rings of Finite Section in Incompressible Fluids" *Bull. Cal. Math. Soc.*, Vol. 13, p. 117, 1922.

<sup>2</sup> Kelvin—"Collected Scientific papers," Vol. 4, p. 67.

<sup>3</sup> Hicks—"Phil. Trans A," Vol. 175, 1884; also Vol. 176, 1885.

<sup>4</sup> Chree—"Proc. Edin. Math. Soc.," Vol. 6, 1888.

<sup>5</sup> Basset—"Hydrodynamics, part II.

<sup>6</sup> Dyson—"Potential of Anchor Ring," parts I and II. *Phil. Trans A*, Vol. 184, 1898.

<sup>7</sup> Thomson—"Motion of Vortex Rings."

Also Gray—"Notes on Hydrodynamics," *Phil. Mag.* (6), Vol. 28, p. 13, 1914.

Lamb—"Hydrodynamics," Ed. IV, 1916.



2. Let  $2\omega$ =vorticity,  $k$ =strength of the vortex

$c$ =radius of the "circular axis"

$\rho, \phi, z$ =cylindrical co-ordinates of any point referred to the centre of the circular axis as origin and the axis of the ring as  $z$ -axis.

$r$ =distance of any point from the circular axis

$\theta$ =inclination of this distance to the plane of the "circular axis," so that  $\rho=c-r \cos \theta$ .

$V$ =velocity of translation of the ring parallel to  $z$ -axis

$$J = \int_0^\pi \frac{c \cos \phi d\phi}{[z'^2 + c^2 - 2c\rho' \cos \phi + \rho'^2]^{\frac{1}{2}}}$$

$a$ =radius of the cross-section.

$$l = \log \frac{8c}{r} - 2, \quad s = \frac{r}{c},$$

$$\lambda = \log \frac{8c}{a} - 2, \quad \sigma = \frac{a}{c},$$

$$\nabla^2 = \frac{d^2}{dc^2} + \frac{d^2}{dz'^2}, \quad \frac{d}{dc} = \nabla \cos \alpha, \quad \frac{d}{dz'} = \nabla \sin \alpha$$

$\psi$ =Stokes' stream function.

Then, it can be proved that at any point  $(\rho', \phi', z')$  outside the vortex filament<sup>1</sup>

$$\begin{aligned} \psi &= \frac{\rho'}{2\pi} \iiint \frac{\omega \rho \cos \phi d\phi d\rho dz}{\{(z'-z)^2 + \rho'^2 - 2\rho\rho' \cos \phi + \rho^2\}^{\frac{1}{2}}} \\ &= \frac{\rho'}{\pi} \iint \omega \left( x \frac{d}{dc} - z \frac{d}{dz'} \right) dx dz J \end{aligned} \quad \dots \quad (1)$$

<sup>1</sup> *Bull. Cal. Math. Soc.*, Vol. 13, p. 120.

where the integral is to be taken over any circular section of the ring.

Now, let

$$\omega = A_0 [1 + A_1 r \cos \theta + A_2 r^2 \cos 2\theta + A_3 r^3 \cos 3\theta + \dots \dots] \quad \dots \quad (2)$$

$$\therefore k = \int_0^{2\pi} \int_0^a 2\omega r dr d\theta = 2\pi a^2 A_0 \quad \dots \quad (3)$$

From (1) and (2), we have

$$\begin{aligned} \psi &= \frac{\rho'}{\pi} \int_0^a \int_0^{2\pi} e^{-r\nabla \cos(\theta-a)} A_0 (1 + A_1 r \cos \theta + A_2 r^2 \cos 2\theta + \dots) r dr d\theta J. \\ &= \frac{\rho' A_0}{\pi} \int_0^a \int_0^{2\pi} \{ I_0(r\nabla) - 2I_1(r\nabla) \cos(\theta-a) + 2I_2(r\nabla) \cos 2(\theta-a) + \dots \} \\ &\quad \times \{ 1 + A_1 r \cos \theta + A_2 r^2 \cos 2\theta + \dots \dots \} r dr d\theta J. \end{aligned}$$

where  $I_n$  is Bessel Function of the  $n^{th}$  order with imaginary modulus.

$$= \frac{k\rho'}{\pi a^2} \left[ \frac{a}{\nabla} I_1(a\nabla) - A_1 \cos a \frac{a^2}{\nabla} I_2(a\nabla) + A_2 \cos 2a \frac{a^3}{\nabla} I_3(a\nabla) - \text{etc.} \right] J$$

$$\left[ \because \int_0^a r^{n+1} I_n(r\nabla) dr = \frac{a^{n+1}}{\nabla} I_{n+1}(a\nabla) \right]^1$$

$$= \frac{k\rho'}{2\pi} \left[ 1 + \frac{a^2 \nabla^2}{8} + \frac{a^4 \nabla^4}{192} + \frac{a^6 \nabla^6}{3072} + \dots \dots \right]$$

$$- \frac{A_1}{4} \cos a \nabla a^2 \left( 1 + \frac{a^2 \nabla^2}{12} + \frac{a^4 \nabla^4}{384} + \dots \dots \right)$$

$$\begin{aligned}
& + \frac{A_2 a^4}{24} \nabla^2 \cos 2\alpha \left( 1 + \frac{a^2 \nabla^2}{16} + \frac{a^4 \nabla^4}{640} + \dots \dots \right) \\
& - \frac{A_3 a^6}{192} \nabla^3 \cos 3\alpha \left( 1 + \frac{a^2 \nabla^2}{20} + \dots \dots \right) \dots \dots \left. \right] J \\
= & \frac{k\rho'}{2\pi} \left[ 1 + \left( \frac{a^2}{8} - \frac{A_1 a^2 c}{4} + \frac{A_2 a^4}{24} \right) \frac{1}{c} \frac{d}{dc} \right. \\
& + \left\{ -\frac{a^4}{192} - \frac{A_1 a^4 c}{48} + A_2 a^4 \left( \frac{c^2}{12} + \frac{a^2}{384} \right) \right. \\
& \left. \left. - \frac{3A_3 a^6 c}{64} \right\} \left( \frac{1}{c} \frac{d}{dc} \right)^2 + \left\{ \frac{a^6}{3072} + \frac{A_1 a^6 c}{1536} \right. \right. \\
& \left. \left. + \frac{A_2 a^6}{192} \left( c^2 - \frac{a^2}{80} \right) - \frac{A_3 a^6 c^3}{48} \left( 1 + \frac{9a^2}{80} \right) \right\} \left( \frac{1}{c} \frac{d}{dc} \right)^3 \text{ etc.} \right] J \quad (4)^1
\end{aligned}$$

Now,

$$\begin{aligned}
J \frac{\rho'}{c} = & l - \frac{l+1}{2} s \cos \theta + \left( \frac{2l+5}{16} - \frac{l}{16} \cos 2\theta \right) s^2 \\
& + \left( \frac{3l+5}{64} \cos \theta - \frac{3l-1}{192} \cos 3\theta \right) s^3 \\
& + \left( \frac{12l+11}{2048} + \frac{12l+17}{768} \cos 2\theta - \frac{15l-8}{3072} \cos 4\theta \right) s^4 + \text{etc.} \dots \quad (5)^2 \\
\frac{\rho'}{c} \left( \frac{1}{c} \frac{d}{dc} \right) J = & \frac{1}{c^2 s} \left\{ -\cos \theta + \left( \frac{2l+3}{4} + \frac{\cos 2\theta}{4} \right) s \right. \\
& + \left( \frac{4l+1}{32} \cos \theta + \frac{\cos 3\theta}{32} \right) s^2 + \left( -\frac{4l+7}{128} + \frac{4l+1}{64} \cos 2\theta \right. \\
& \left. \left. + \frac{\cos 4\theta}{128} \right) s^3 + \text{etc.} \right\} \dots \quad (6)
\end{aligned}$$

<sup>1</sup> For simplification, see *Bull. Cal. Math. Soc.*, Vol. 13, p. 124.

<sup>2</sup> Dyson—"Phil. Trans.," *Ibid*, part I, p. 54; part II, pp. 1086-87.

$$\frac{\rho'}{c} \left( \frac{1}{c} \frac{d}{dc} \right)^3 J = \frac{1}{c^3 s^3} \left\{ \cos 2\theta - \frac{\cos \theta + \cos 3\theta}{4} s \right. \\ \left. - \left( \frac{12l+9}{32} + \frac{\cos 2\theta}{4} + \frac{\cos 4\theta}{32} \right) s^2 + \text{etc.} \right\} \quad \dots \quad 7.$$

$$\frac{\rho'}{c} \left( \frac{1}{c} \frac{d}{dc} \right)^3 J = -\frac{1}{c^3 s^3} \left\{ 2 \cos 3\theta + \left( \cos 2\theta - \frac{\cos 4\theta}{2} \right) s + \dots \right\} \quad (8)$$

$$\frac{\rho'}{c} \left( \frac{1}{c} \frac{d}{dc} \right)^4 J = \frac{1}{c^3 s^4} \left\{ 6 \cos 4\theta + \dots \right\} \quad \dots \quad (9)$$

etc.,                      etc.,                      etc.

Hence on the surface of the vortex ring, we have, after substitution and simplification,

$$\psi = \frac{kc}{2\pi} \left[ \text{const.} - \left\{ \frac{(\lambda+1)}{2} \sigma - \frac{3\lambda+5}{64} \sigma^3 \right. \right. \\ \left. \left. + \left( \frac{1}{8} - \frac{A_1 c}{4} + \frac{A_2 a^2}{24} \right) \left( 1 - \frac{\sigma^2}{32} (4\lambda+1) \right) \sigma \right. \right. \\ \left. \left. + \frac{\sigma^3}{4} \left( -\frac{1}{192} - \frac{A_1 c}{48} + \frac{A_2 c^2}{12} - \frac{3A_3 a^2 c}{64} \right) \right\} \cos \theta \right. \\ \left. - \left\{ \frac{\lambda}{16} \sigma^2 - \frac{\sigma^2}{4} \left( \frac{1}{8} - \frac{A_1 c}{4} + \frac{A_2 a^2}{24} \right) \right. \right. \\ \left. \left. + \left( \frac{1}{192} + \frac{A_1 c}{48} - \frac{A_2 c^2}{12} + \frac{3A_3 a^2 c}{64} \right) \sigma^2 \right\} \cos 2\theta \right. \\ \left. - \left\{ \frac{(3\lambda-1)}{192} - \frac{1}{32} \left( \frac{1}{8} - \frac{A_1 c}{4} + \frac{A_2 a^2}{4} \right) \right. \right. \\ \left. \left. - \left( \frac{1}{192} + \frac{A_1 c}{48} - \frac{A_2 c^2}{12} + \frac{3A_3 a^2 c}{64} \right) \frac{1}{4} \right. \right. \\ \left. \left. + \left( \frac{1}{1536} + \frac{A_1 c}{768} + \frac{A_2 c^2}{96} - \frac{A_3 c^3}{24} \right) + \text{etc} \right\} \sigma^3 \cos 3\theta + \dots \right] \quad (10)$$

Further, let us suppose that the "centroid" of the vortex filament lies on the "circular axis" of the ring. In that case we must have

$$\int_0^{2\pi} \int_0^a \omega r \cos \theta r dr d\theta = 0$$

Hence from (2), we have  $A_1 = 0$  ... (11)

Also, from the boundary condition for a velocity of translation  $V$  parallel to  $z$ -axis, we have

$$\begin{aligned} \psi &= \frac{V\rho^2}{2} + \text{constant on the surface of the ring} \\ &= \left[ \text{constant} - Vac \cos \theta + \frac{Va^2}{4} \cos 2\theta \right] \end{aligned}$$

Hence, from this and (10), by equating co-efficients of  $\cos \theta$ , etc. (always neglecting quantities of the order  $\sigma^4$  and higher powers of  $\sigma$ ), we have

$$\frac{k}{2\pi c} \left\{ \frac{\lambda+1}{2} - \frac{3\lambda+5}{64} \sigma^2 + \frac{1}{8} + \frac{A_2 a^2}{24} - \frac{\sigma^2}{256} (4\lambda+1) \right.$$

$$\left. - \frac{\sigma^2}{4} \left( \frac{1}{192} - \frac{A_2 c^2}{12} \right) \right\} = V \quad \dots (12)^1$$

$$\frac{k}{2\pi c} \left\{ -\frac{\lambda}{16} + \frac{1}{32} - \frac{1}{192} + \frac{A_2 c^2}{12} \right\} = \frac{V}{4} \quad \dots (13)$$

<sup>1</sup> In obtaining results (12) to (14),  $A_2 a^2$ ,  $A_2 c^2$  have been supposed (it will be proved afterwards, see results (16) and (17)) to be of the order  $\sigma^2$ ,  $\sigma^2$  respectively.

$$\frac{3\lambda-1}{192} - \frac{1}{256} - \frac{1}{768} + \frac{A_2 c^2}{48} + \frac{1}{1536} + \frac{A_2 c^2}{96} - \frac{A_3 c^3}{24} = 0 \quad \dots (14)$$

Solving for  $V, A_2, A_3,$

we obtain

$$V = \frac{k}{2\pi c} \left[ \frac{4\lambda+5}{8} + \frac{60\lambda+11}{768} \sigma^2 \right] \quad \dots (15)$$

$$A_2 c^2 = \frac{36\lambda+25}{16} + \frac{60\lambda+11}{256} \sigma^2 \quad \dots (16)$$

$$A_3 c^3 = \frac{33\lambda+15}{16} + \frac{180\lambda+33}{1024} \sigma^2 \quad \dots (17)$$

Since, we neglect terms containing  $\sigma^2$  in  $A_2 c^2$  and  $A_3 c^3$  in writing down equations (13) and (14), it will be more correct to reject terms containing  $\sigma^2$  in (16) and (17).

$\therefore$  From (2), we have, at any point  $(r, \theta)$  of the vortex filament,

$$\omega = \frac{k}{2\pi a^2} \left[ 1 + \frac{r^2}{c^2} \left( \frac{36\lambda+25}{16} \right) \cos 2\theta + \frac{r^3}{c^3} \frac{33\lambda+15}{16} \cos 3\theta \dots \right] \quad \dots (18)$$

Here, we have found vorticity correct to  $\sigma^3$ . The above method of treatment may be extended to find  $\omega$  correct to higher powers of  $\sigma$

4. From (15) the velocity to a first approximation is given by

$$V = \frac{k}{16\pi c} (4\lambda+5) = \frac{k}{4\pi c} \left( \log \frac{8c}{a} - \frac{3}{4} \right)$$

This is identical with the velocity of translation<sup>1</sup> of a ring of variable section whose vorticity is constant. The result might have

<sup>1</sup> See result (27) *Bull. Cal. Math. Soc.*, p. 127, Vol. 13.

been expected, inasmuch as if we neglect  $\sigma^2$  and higher powers, the vorticity is found from (18) to be

$$\omega = \frac{k}{2\pi a^2} = \text{constant over the cross section.}$$

Hence, the velocity of translation must be same as that of a ring with constant vorticity at least to this order of approximation.

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## NOTE ON THE CONVERGENCE OF FOURIER'S SERIES.

The criteria of convergence of Fourier's series have been studied among others, by Dini, Jordan and De la Vallée Poussin; and certain isolated conditions (which are sufficient but not necessary) have been suggested by them. The condition proposed by the last is the most general of all; the proof of its greater generality, however, is not given in his "Course d'Analyse" (Ed. 1922, Tome II). The following proof was obtained by the writer while preparing for the Tripos. The proof becomes so short by the use of the property that an indefinite integral is of bounded variation according to both Riemann and Lebesgue.

It is assumed that  $f(x)$  and its absolute value are integrable, either in the sense of Riemann or Lebesgue. We have,

$$\phi(\theta) = f(x+\theta) + f(x-\theta) - 2s, \text{ where } s \text{ is properly chosen.}$$

### I. *Dini's condition.*

If  $\frac{|\phi(\theta)|}{\theta}$  is integrable in the neighbourhood of '0', the Fourier's series of  $f(x)$  converge towards  $f(x)$ . Here  $s = f(x)$ .

### II. *Jordan's condition.*

The Fourier's series of  $f(x)$  converge to  $\frac{1}{2}[f(x+0) + f(x-0)]$  at every point in the neighbourhood of which  $f(x)$  is of bounded variation.

Here,  $s = \frac{1}{2}[f(x+0) + f(x-0)]$  at all points of discontinuity of the first kind,  $f(x+0)$ ,  $f(x-0)$  being equal to  $f(x)$  at all points of regularity.

### III. *De la Vallée Poussin's condition.*

The Fourier's series of  $f(x)$  converge to  $s$

where

$$\Phi_1(\alpha) = \frac{1}{\alpha} \int_0^\alpha \phi(\theta) d\theta$$

is of bounded variation in the neighbourhood of '0';  $s$  being so chosen that  $\Phi_1(\alpha) \rightarrow 0$  as  $\alpha \rightarrow 0$ .



*Proof.*

A. By Dini's condition

since  $\int_0^a \left| \frac{\phi(\theta)}{\theta} \right| d\theta$  exists,  $a$  being small;  $\lambda(a) = \int_0^a \frac{\phi'(\theta)}{\theta} d\theta$  does,

and  $\lambda'(a) = \frac{\phi(a)}{a}$ .

Now

$\Phi_1(a) = \frac{1}{a} \int_0^a \phi(\theta) d\theta = \frac{1}{a} \int_0^a \theta \lambda'(\theta) d\theta$  is of bounded variation by the

property of an indefinite integral provided  $\Phi_1(0) = 0$ .

$$\Phi_1(a) = \frac{1}{a} \left[ a\lambda(a) - \int_0^a \lambda(\theta) d\theta \right] \leq \lambda(a) - \lambda(a_1)$$

where  $\lambda(a_1)$  is  $\max \lambda(a)$  in  $0 < a_1 < a$ .

But the expression on the right hand side  $\rightarrow 0$  with  $a$ , by Dini's condition

$$\Phi_1(0) = 0.$$

Thus if Dini's condition is satisfied, De la Vallée Poussin's is also satisfied.

B. By Jordan's condition  $\Phi(a) \rightarrow 0$  with  $a$  and is continuous near  $a$ .

$\therefore$  by the property of an indefinite integral  $\int_0^a \phi(a) d\theta$  is of bounded

variation and consequently  $\Phi_1(a)$ .

The only step to prove is that  $\Phi_1(\alpha) \longrightarrow 0$  with  $\alpha$ .

Now,

$$\lim \Phi_1(\alpha) = \lim_{\alpha \longrightarrow 0} \frac{\Phi(\alpha) - \Phi(0)}{\alpha}, \quad \text{where } \Phi(\alpha) = \int_0^\alpha \phi(\theta) d\theta$$

$$= \Phi'(0) = \phi(0), \quad \text{by Jordan's condition.}$$

$\therefore$  if Jordan's condition is satisfied so is De la Vallée Poussin's.

K. C. D.

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# SUR LA DISTANCE DE DEUX ENSEMBLES

PAR

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*Introduction.*—Dans une note “Sur les ensembles mesurables” publiée dans les Comptes Rendus de l’Académie des Sciences, 1923, page 69, M. Tade Wazewski obtient un certain nombre de propriétés des suites d’ensembles mesurables en appliquant une définition de la distance de deux ensembles mesurables qu’il attribue à M. Nikodym.

Je me propose de montrer ici comment les résultat de M. Wazewski et de M. Nikodym peuvent être considérés comme cas particuliers de propositions que j’ai obtenu précédemment concernant les suites de fonctions mesurables. Il suffira pour cela de supposer qu’on limite ces propositions au cas où les fonctions qu’on considère ne peuvent prendre que les valeurs zéro et un. Alors chacune de ces fonctions pourra être considérée comme la “fonction caractéristique” d’un ensemble—mesurable en même temps que la fonction—à savoir la fonction égale à un sur cet ensemble et nulle en dehors.

*Distance de deux ensembles.*—Dans certaines théories, l’influence d’un ensemble est pour ainsi dire massique ; il importe peu qu’on enlève ou qu’on ajoute un point à cet ensemble ; il importe même peu qu’on lui enlève ou qu’on lui ajoute une infinité de points pourvu que tous ceux-ci restent compris dans un ensemble de mesure nulle. C’est en vue de l’utilisation de nos résultats dans ces théories que nous allons nous placer.

Nous avons convenu de considérer deux fonctions comme non distinctes lorsqu’elles ne diffèrent que dans un ensemble de mesure nulle. Si ces deux fonctions sont les fonctions caractéristiques de deux ensembles linéaires  $E, F$ , cela revient à dire que l’ensemble des points de  $E$  qui n’appartiennent pas à  $F$  et des points de  $F$  qui n’appartiennent pas à  $E$  est de mesure nulle.

Ainsi on ne considérera pas comme distincts deux ensembles  $E, F$  tels que

$$\text{mesure de } [(E-F) + (F-E)] = 0.$$

II Nous avons défini<sup>1</sup> la distance de deux fonctions  $f(x), \phi(x)$  comme la borne inférieure  $(f, \phi)$  de la somme

$$w + m_w$$

quand  $w$  varie en restant positif, en désignant par  $m_w$  la mesure extérieure au sens de M. Lebesgue de l'ensemble des points où  $|f(x) - \phi(x)| > w$ . Si  $f, \phi$  sont les fonctions caractéristiques de deux ensembles  $E, F$  on voit que si  $w \leq 1$ ,  $m_w = 0$ , donc  $w + m_w$  reste supérieur ou égal à un et si  $1 > w > 0$ ,  $m_w$  est la mesure extérieure  $\mu$  de l'ensemble  $(E - F) + (F - E)$  de sorte que  $w + m_w = w + \mu$  est aussi voisin que l'on veut de  $\mu$  en prenant  $w$  assez petit. Si l'on suppose<sup>2</sup> que l'intervalle de définition des fonctions est l'intervalle  $(0, 1)$ , on voit que la borne inférieure de  $w + m_w$  est égal à  $\mu$ . Finalement si on convient d'appeler distance de  $E$  à  $F$  et de représenter par  $(E, F)$  la distance de leurs fonctions caractéristiques, on aura

$$(E, F) = \text{mesure extérieure de } [(E - F) + (F - E)]$$

Il résulte alors des propriétés démontrées<sup>2</sup> pour la distance  $(f, \phi)$  que la distance de deux ensembles jouit des propriétés suivants.

I La condition nécessaire et suffisante pour que deux ensembles linéaires  $E, F$  ne diffèrent chacun de leur ensemble commun que par un ensemble de mesure nulle est que leur distance  $(E, F)$  soit nulle.

II On a  $(E, F) = (F, E)$ . Et si l'on substitue à  $E, F$  deux ensembles  $E_1, F_1$  équivalents au sens précédent à  $E, F$ , on a

$$(E_1, F_1) = (E, F)$$

III Quels que soient les ensembles linéaires  $E, F, G$ , on a

$$(E, F) \leq (E, G) + (G, F)$$

Seulement on remarquera que si notre définition coïncide avec celle de M. Nikodym dans le cas, visé par celui-ci, où les ensembles linéaires considérés sont mesurables, elle subsiste et vérifie encore les conditions I, II, III pour des ensembles linéaires quelconques.

*Élément-limite.*—Dans le mémoire cité plus haut, nous établissions que la classe des fonctions quelconques d'une variable numérique  $x$  est une classe (D), c'est à dire qu'on peut y définir une distance compatible avec la définition de la convergence des suites de fonctions si l'on a choisi pour celle-ci la convergence *en mesure* de F. Riesz—généralisée au cas des fonctions quelconques.

<sup>1</sup> Bull. Calcutta Math. Soc., Vol. XI, 1921.

<sup>2</sup> Dans le cas contraire, on prendrait pour fonction caractéristique d'un ensemble une fonction égale sur l'ensemble à la longueur de l'intervalle.

Nous avons donc en somme prouvé une propriété importante d'une définition de la convergence introduite précédemment et qui a rendu des services en Analyse.

Si au contraire, on introduit a priori comme M. Nikodym une définition de la distance de deux fonctions mesurables, on ne prouve pas par là qu'une telle définition est possible ; cela est possible dans toute classe et d'une infinité de manières ; ce qui n'est pas toujours possible c'est de définir une distance compatible avec une définition de la limite donnée. Mais inversement on introduit par la même une définition de la convergence d'une suite et il est utile de voir en qui consiste cette convergence, ou ce qui sont ses propriétés.

D'après la façon dont nous avons opéré on voit que si l'on convient qu'une suite d'ensembles linéaires  $E_1, E_2, \dots$  converge vers un ensemble  $E$  lorsque la distance  $(E, E_n)$  tend vers zéro, on retombe sur un cas particulier de la convergence en mesure de F. Riesz. Comment se traduit-il lorsque les fonctions considérées par F. Riesz sont des fonctions caractéristiques d'ensemble ?

La condition nécessaire et suffisante pour que la distance  $(E, E_n)$  des deux ensembles linéaires  $E$  et  $E_n$ , converge vers zéro avec  $\frac{1}{n}$  est que les points de  $E$  et de  $E_n$  qui ne sont pas communs à ces deux ensembles puissent être enfermés dans un ensemble dénombrable  $I_n$  d'intervalles dont la longueur totale tend vers zéro avec  $\frac{1}{n}$ .

Il y a lieu de faire remarquer que l'ensemble  $I_n$  d'intervalles est variable avec  $n$  et en outre que si la mesure de  $I_n$  tend vers zéro, l'ensemble commun aux  $I_n$  n'est pas nécessairement de mesure nulle. Enfin les ensembles limite complet et restreint,  $C$  et  $R$ , des ensembles  $E_n$ , peuvent aussi différer sur un ensemble de mesure non nulle. L'exemple donné dans le mémoire précédemment cité relatif au cas des fonctions s'adapte immédiatement au cas des ensembles. Divisons l'intervalle fixe  $J$  où sont situés les ensembles considérés en 2 intervalles égaux  $J_1, J_2$ , puis en 4 intervalles égaux  $J_1, J_2, J_3, J_4$ , puis en huit, et.

Prenons alors pour ensemble  $E_n$  l'intervalle  $J_n$  ; il est manifeste que la suite des distances des  $J_n$  à l'ensemble  $E$  vide de tout point tend vers zéro. Pourtant l'ensemble limite complet des  $J_n$  est constitué par l'intervalle fondamental  $J$  tout entier, alors que leur ensemble limite restreint est vide comme  $E$ .

Il est par contre toujours possible d'extraire d'une suite d'ensembles  $E_n$  qui convergent en mesure vers un ensemble  $E$  une suite particulière  $E_{n_1}, E_{n_2}, \dots$  pour laquelle non seulement les ensembles limites complet et restreint de cette suite particulière coïncident à un ensemble de

mesure nulle près, mais encore telle que les ensembles d'exclusion  $I_{n,1}$ ,  $I_{n,2}, \dots$  soient chacun compris dans le précédent.

En d'autres termes il est possible de choisir parmi les  $E_n$ , une suite particulière  $E_{n,1}$ ,  $E_{n,2}$ , telle que quel que soit  $E$  il existe un ensemble d'intervalles de longueur totale inférieure à  $E$  et en dehors desquels les  $E_n$  sont identiques (et identiques à  $E$ ) à partir d'un certain rang.

Cette proposition s'obtient immédiatement en appliquant au cas des fonctions caractéristiques un théorème concernant les suites de fonctions convergeant en mesure, théorème démontré d'abord par F. Riesz pour les fonctions mesurables et étendu dans mon mémoire aux fonctions quelconques d'une variable.

Il résulte en particulier de ce qui précède que les ensembles limites complet et restreint  $C'$  et  $R'$  de la suite des  $E_n$  sont identiques à un ensemble près de mesure nulle ce qui constitue la proposition IV de M. Wazewski. Mais la proposition actuelle est plus précise.

Enfin la proposition II de M. Wazewski s'obtient immédiatement si l'on applique aux fonctions caractéristiques d'ensembles, le résultat démontré dans mon mémoire concernant la condition de convergence en mesure d'une suite de fonctions. On peut alors dire que :

Pour qu'une suite d'ensemble,  $E_1, E_2, \dots$  converge en mesure il faut et il suffit que quel que soit  $E$  la distance  $(E_n, E_{n+p})$  de l'un  $E_n$  de ces ensembles à l'un quelconque  $E_{n+p}$  des suivants, soit inférieure à  $E$  quel que soit  $p$ , pour  $n$  assez grand.

Autrement dit, quand on définit la convergence d'une suite d'ensembles par la convergence en mesure, la classe des ensembles linéaires est une classe (D) complète.

.—D'autre part, j'ai montré ailleurs quelle importance ont pour une classe (D) certaines propriétés générales qui permettent d'étendre à cette classe un grand nombre de théorèmes de la théorie des ensembles linéaires. Établissons ici certaines de ces propriétés pour la classe des ensembles linéaires.

.—D'abord cette classe est évidemment parfaite. Autrement dit quel que soit l'ensemble linéaire  $E$  il existe un ensemble  $F$  distinct de  $E$  au sens adopté plus haut et dont la distance à  $E$  est aussi petite que l'on veut. Il suffit pour former  $F$  d'ajouter à  $E$  ou de supprimer de  $E$ , suivant le cas, un intervalle de longueur aussi petite qu'on voudra.

.—On peut aussi joindre deux éléments d'un même sphéroïde par un arc de Jordan contenu dans ce sphéroïde.

Autrement dit si l'on considère deux ensembles linéaires  $E, F$  dont les distances à un ensemble  $C$  sont au plus égales à  $\rho$ , il est possible de définir

un ensemble linéaire  $G_t$ , dépendant d'un paramètre  $t$  de sorte que  $G_0 = E$ ,  $G_1 = F$ , que  $(C, G_t) \leq \rho$  pour  $0 \leq t \leq 1$  et enfin tel que  $(G_t, G_{t'})$  tende vers zéro quand  $(t' - t)$  tend vers zéro.

Il suffit évidemment de montrer que cela est possible quand l'un des éléments  $E, F$ ;— $F$  par exemple—est au centre du sphéroïde. Car alors il suffira dans le cas général de joindre  $E$  à  $C$  et  $C$  à  $F$ .

Or considérons l'ensemble

$$U = (E - C) + (C - E)$$

et l'ensemble  $U$ , des points de  $E - C$  qui sont situés dans l'intervalle  $0, t$ , et de  $C - E$  qui sont situés dans l'intervalle  $(t, 1)$ . On a :

$U_0 = C - E$  et  $U^1 = E - C$  ; donc en posant  $G_t = C, E + U_t$ , on aura

$$G_0 = C \text{ et } G_1 = E$$

D'autre part l'ensemble  $(C - G_t) + (G_t - C)$  se compose de la partie de  $(C - E)$  comprise dans  $(0, t)$  et de la partie de  $E - C$  comprise de  $0$  à  $t$ . Donc la distance  $(C, G_t)$  croît constamment ou du moins ne décroît pas quand  $t$  croît ; ses valeurs extrêmes sont  $0$  et  $(C, G_1) = (C, E) \leq \rho$ . Finalement  $G_t$  reste bien compris dans le sphéroïde de centre  $C$ . Enfin,  $(G_t - G_{t'}) + (G_{t'} - G_t)$  est un ensemble compris dans l'intervalle  $(t, t')$ , par conséquent

$$(G_t, G_{t'}) \leq (t' - t)$$

et l'élément  $G_t$  dépend continuellement de  $t$ .

.—Donc ce qui précède s'applique à des ensembles linéaires quelconques. Nous voyons ainsi que lorsqu'on adopte pour définition de la convergence d'une suite d'éléments la convergence en mesure, la classe des ensembles linéaires est une classe (D) parfaite, complète et où deux éléments quelconques d'un sphéroïde peuvent être joints par un arc de Jordan appartenant à ce sphéroïde. Cette classe possède donc toutes les propriétés que j'ai énoncées concernant les classes de cette espèce dans mon mémoire "Esquisse d'une théorie des ensembles abstraits, University of Calcutta, 1922."

.—*Cas des ensembles mesurables.*—Il en est de même dans le cas où on restreint la classe aux ensembles linéaires mesurables. Il suffit en effet de remarquer que dans les démonstrations précédentes, si on suppose que les ensembles donnés sont mesurables, les ensembles construits à partir de ceux-ci et utilisés dans ces démonstrations sont aussi mesurables.

Mais on peut énoncer en outre une propriété spéciale à la classe des ensembles linéaires mesurables, à savoir que cette classe est séparable. Nous avons indiqué en effet dans le second mémoire cité (page 389)



que la classe des fonctions mesurables peut être considérée comme l'ensemble dérivé d'un de ses ensembles dénombrables, à savoir l'ensemble des fonctions qui sont constantes et de valeurs rationnelles dans chacune des sub-divisions de l'intervalle fondamental limitées par un nombre fini variable de points d'abscisses rationnelles. Dans le cas où on prend comme fonction des fonctions caractéristiques d'ensembles, on voit que la classe des ensembles mesurables peut être considérée comme l'ensemble dérivé de l'ensemble dénombrable  $N$  dont chaque élément est l'ensemble linéaire mesurable constitué par la réunion d'un nombre fini d'intervalles à extrémités rationnelles. C'est en utilisant également l'ensemble dénombrable  $N$  que la même proposition a été établie par M. Wazewski.

.—Il est alors loisible d'appliquer à la classe des ensembles mesurables le même théorème que j'ai démontré pour les fonctions mesurables. Tout ensemble (d'ensembles linéaires mesurables) est condensé. En effet nous savons que cela est vrai pour tout ensemble tiré d'une classe (D) séparable.

Je rappelle la signification du théorème obtenu. Etant donné un ensemble quelconque  $F$  d'ensembles linéaires mesurables, tout sous-ensemble non dénombrable  $G$  de  $F$  donne lieu à au moins un élément de condensation  $E$ . C'est à dire qu'il existe un ensemble linéaire mesurable  $E$  qui est élément limite d'une suite convergeant en mesure d'ensembles tirés de  $G$  et aussi d'une suite convergeant en mesure d'ensemble tirés de  $G - N$  quel que soit le sous-ensemble dénombrable  $N$  de  $G$ .

.—Il en résulte en particulier ce corollaire que : de tout ensemble non dénombrable d'ensemble linéaires mesurables on peut tirer une suite convergeant en mesure ; et comme de celle-ci on peut extraire une suite d'ensembles satisfaisant à la condition plus précise indiquée plus haut, on peut dire en résumé.

De tout ensemble non dénombrable  $F$  d'ensembles linéaires mesurables, on peut tirer une suite d'ensembles  $F_1, F_2, \dots, F_n, \dots$  qui coïncident entre eux à partir de chaque rang  $n$  en dehors d'un ensemble  $I_n$  composé d'une suite dénombrable d'intervalles dont la longueur totale tend vers zéro avec  $\frac{1}{n}$ ,  $I_{n+1}$ , étant compris dans  $I_n$ .

Il en résulte en particulier que l'ensemble limite complet et l'ensemble limite restreint des  $F_n$  coïncident en dehors d'un ensemble de mesure nulle (l'ensemble commun aux  $I_n$ )—ce qui donne la proposition I de M. Wazewski moins précise que la précédente.

.—*Examen de diverses définitions de la convergence.*—Dans ce qui précède nous avons admis qu'on prenait comme définition de la convergence d'une suite d'éléments, la convergence en mesure, l'ensemble

linéaire  $E_n$  convergeant en mesure vers  $E$  si  $E_n$  et  $E$  coïncident en dehors d'un ensemble dénombrable  $I_n$  d'intervalles dont la longueur totale tend vers zéro avec  $\frac{1}{n}$ . Nous avons vu que dans ces conditions, on peut définir la convergence par l'intermédiaire d'une distance.

D'autres définitions de la convergence paraîtraient plus naturelles et il est important de montrer qu'elles ont l'inconvénient de ne pas représenter à l'intermédiaire d'une distance, en même d'un écart.

Par exemple on pourrait dire que  $E_n$  converge si ses ensembles limites complet et restreint coïncident. Mais si l'on adoptait une telle définition et si elle pourrait se traduire par l'intermédiaire d'une distance tout ensemble dérivé d'un ensemble d'ensembles linéaires serait fermé. Or nous savons qu'il n'en est pas ainsi ; car en partant par exemple de l'ensemble  $E$  des ensembles linéaires formés d'un nombre fini d'intervalles, on trouve comme ensembles dérivé  $E'$ , un ensemble d'ensembles linéaires qui n'est pas fermé !

On ne pourrait même pas traduire la définition actuelle de la convergence par l'intermédiaire d'un "écart." Autrement dit, quel que soit la façon dont on ferait correspondre à tout couple d'ensembles linéaires  $E, F$  un nombre  $[E, F]$  qu'on appellerait écart de  $E, F$ , il serait impossible de satisfaire aux conditions suivantes :

- I  $[E, F]=0$  est la condition nécessaire et suffisante pour que  $E, F$  coïncident.
- II Quels que soient  $E, F$ , on a  $[E, F]=[F, E] \geq 0$ .
- III La condition nécessaire et suffisante pour que  $[E, E_n]$  tende vers zéro est que les ensembles limites complet et restreint de  $E_n$ , coïncident avec  $E$ .

En effet, désignons par  $V_q$  l'ensemble de point communs à tous les ensembles  $F$  tels que  $[E, F] < \frac{1}{q}$ . Parmi ces ensembles  $F$  figure  $E$  lui même, donc  $V_q$  est compris dans  $E$ , quelque soit  $q$ . Ainsi  $E$  comprend  $V_1 + V_2 + \dots$ ; ces deux ensembles sont même identiques ; car si un point  $x$  de  $E$  n'appartenait pas à  $V_1 + V_2 + \dots$  il n'appartiendrait pas par exemple à  $V_q$ . Si donc on considère une suite  $E_1, E_2, \dots$  convergeant vers  $E$ , comme  $[E, E_n]$  tend vers zéro on aurait  $[E, E_n] < \frac{1}{q}$  pour  $n$  assez grand par exemple  $n > p$ . Donc les  $E_n$  comprendrait  $V_q$  à partir du rang  $n=p+1$ , et par suite  $x$  n'étant compris dans aucun des ensembles  $E_{p+1}, E_{p+2}, \dots$  ne pourrait être compris dans leur ensemble-limite  $E$ , contrairement à l'hypothèse. Ainsi.

$$E = V_1 + V_2 + \dots$$

Ceci étant prenons pour  $E$  un ensemble non dénombrable. Alors  $V_1, V_2, \dots$  ne pourront ne contenir chacun qu'un nombre fini de points. On

pourra donc choisir une infinité de points distincts  $x_1, x_2, \dots, x_n, \dots$  dans l'un au moins de ces ensembles par exemple dans  $V_r$ .

Considerons alors les ensembles  $F_n = E - x_n$ ; ils ont évidemment  $E$  pour ensemble limite complet et restreint. Donc pour  $n$  assez grand, par exemple pour  $n \geq m$ , on aura  $[E, E_n] < \frac{1}{2}$ , alors  $V_r$  sera compris dans  $E_m, E_{m+1}, \dots$  et on arrive à une contradiction puisque  $x_m$  est compris dans  $V_r$  sans l'être dans  $E_m$ .

Ainsi l'hypothèse de l'existence d'un écart doit être écartée :

*Convergent presque uniforme.*—Nous avons suivi ici pour le cas des ensembles la méthode qui nous a réussi dans notre premier mémoire de Calcutta concernant la convergence ordinaire des fonctions. Operons de même pour la convergence presque uniforme.

Celle-ci semble plus naturelle et plus utile que la convergence en mesure et pourtant on la rencontre plus exceptionnellement. Elle consiste en ceci : une suite d'ensembles linéaires  $E_1, E_2, \dots$  converge vers  $E$  si quel que soit  $E$ , on peut assigner un ensemble dénombrable d'intervalles de longueur totale inférieure à  $E$  tel qu'en dehors de cet ensemble d'intervalles les ensembles  $E_n$  coïncident avec  $E$  à partir d'un certain rang.

Montrons qu'on arrive à une contradiction si l'on essaie de définir cette convergence presque uniforme au moyen d'un écart.

Divisons comme précédemment l'intervalle fondamental  $(0, 1)$  en 2 puis 4 puis 8, ... puis  $2^m$  parties égales, et appelons  $I_m^1, I_m^2, \dots, I_m^n, \dots$  ces  $2^m$  parties.

Il est manifeste comme nous l'avons fait déjà remarquer que la suite  $I_2^1, I_2^2, I_4^1, I_4^2, I_4^3, I_4^4, \dots, I_m^n, I_m^{n+1}, \dots$  ne converge uniformément vers aucun ensemble. En particulier elle ne converge pas uniformément vers un ensemble vide et par suite l'écart  $[I_m^n, 0]$  ne tend pas vers zéro. Si l'on appelle  $k_m$  le plus grand de ces écarts pour  $m$  fixe,  $k_m$  ne tend donc pas vers zéro. Autrement dit, il existe un nombre  $\lambda > 0$  tel qu'une infinité des  $k_m$ , soit  $k_{m_1}, k_{m_2}, k_{m_p}, \dots$  restent supérieurs à  $\lambda$ . Soit alors  $J_p$  celui des intervalles  $I_{m_p}^n$  dont l'écart avec zéro est  $k_{m_p}$  et  $C_p$  son centre. On peut extraire de la suite des  $C_p$  une suite convergente,  $C'_1, C'_2, \dots, C'_r, \dots$ ; soit  $C$  son point limite; appelons  $J'_1, J'_2, \dots$  les intervalles  $J_p$  correspondant à  $C'_1, C'_2, \dots$ . Quel que soit le nombre  $\epsilon > 0$ , on peut toujours prendre  $p$  assez grand ( $p > r$ ) pour que  $C'_p$  et même  $J'_p$  soient situés dans un intervalle de centre  $C$  de longueur  $\epsilon$ . Par conséquent la suite des  $J'_p$  converge presque uniformément vers un ensemble nul. Donc  $[J'_p, 0]$  devait tendre vers zéro. Or nous savons que  $[J'_p, 0] > \lambda > 0$ .

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# OSCULATING CONICS FOR THE CURVE $f(x, y) = 0$

By

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An exhaustive treatment of equations of osculating conics of an algebraic curve  $x=F(t)$  and  $y=G(t)$  has been given by Prof. S. Mukhopadhyaya.<sup>1</sup> I have here attempted to extend the results for an algebraic curve given in the form  $f(x, y) = 0$ .

## 1

Let  $f(x, y) = 0$  be the equation of an algebraic curve where  $f(x, y)$  may be supposed to be a rational integral function in  $x$  and  $y$ . Also let the suffixes 1 and 2 denote partial differentiation with respect to  $x$  and  $y$  respectively, i.e., let  $f_1, f_2, f_{11}, f_{12}, f_{22}$ , etc., stand respectively for

$$\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial^2 f}{\partial x^2}, \frac{\partial^2 f}{\partial x \partial y}, \frac{\partial^2 f}{\partial y^2}, \text{ etc.}$$

If as usual  $p, q, r, s$  denote the successive differential co-efficients of  $y$  with respect to  $x$ , we have

$$p = \frac{dy}{dx} = -\frac{f_1}{f_2},$$

$$q = \frac{d^2 y}{dx^2} = \frac{1}{f_2^2} \begin{vmatrix} f_{11} & f_{12} & f_1 \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} = \frac{J}{f_2^2},$$

<sup>1</sup> S. Mukhopadhyaya—A General Theory of Osculating Conics—*Journal and Proceedings, Asiatic Society of Bengal* (New Series), Vol. IV, No. 4, 1908; Vol. IV, No. 10, 1908.

where

$$J \equiv \begin{vmatrix} f_{11} & f_{12} & f_1 \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix};$$

$$r = \frac{d^2 y}{d\epsilon^2} = -\frac{1}{f_2^2} \begin{vmatrix} J_1 & J_2 & 3J \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} = -\frac{K}{f_2^2},$$

where

$$K \equiv \begin{vmatrix} J_1 & J_2 & 3J \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} \text{ and } J_1 = \frac{\partial J}{\partial x}, \quad J_2 = \frac{\partial J}{\partial y};$$

and

$$s = \frac{d^4 y}{d\epsilon^4} = \frac{1}{f_2^3} \begin{vmatrix} K_1 & K_2 & 5K \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix}, \text{ where } K_1 = \frac{\partial K}{\partial x}, \quad K_2 = \frac{\partial K}{\partial y}.$$

Let us further write

$$P \equiv \begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & f_1 \\ f_{21} & f_{22} & f_2 & 2f_1 \cos \omega - f_2 \\ f_1 & f_2 & 0 & 0 \end{vmatrix},$$

$$Q \equiv \begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & 2f_2 \cos \omega - f_1 \\ f_{21} & f_{22} & f_2 & f_2 \\ f_1 & f_2 & 0 & 0 \end{vmatrix},$$

$$R \equiv \begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & f_2 \\ f_{21} & f_{22} & f_2 & f_1 \\ f_1 & f_2 & 0 & 0 \end{vmatrix},$$

$$S = \begin{vmatrix} 1 & \cos \omega & f_1 \\ \cos \omega & 1 & f_2 \\ f_1 & f_2 & 0 \end{vmatrix},$$

$$M = \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_3 \\ f_1 & f_2 & 0 \end{vmatrix}, \quad N = \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_1 \\ f_1 & f_2 & 0 \end{vmatrix},$$

and

$$T = \begin{vmatrix} 1 & \cos \omega & M \\ \cos \omega & 1 & N \\ M & N & 0 \end{vmatrix}.$$

2

The general equation in oblique co-ordinates of a conic passing through two given points  $(x, y)$  and  $(x_1, y_1)$  is of the form

$$\lambda(X-x)(X-x_1) + \mu(Y-y)(Y-y_1) + \nu(X-x)(Y-y_1) + \rho(X-x_1)(Y-y) = 0.$$

If it be a rectangular hyperbola we must have

$$\lambda + \mu - (\nu + \rho) \cos \omega = 0,$$

i.e.,

$$\rho = \frac{\lambda}{\cos \omega} + \frac{\mu}{\cos \omega} - \nu.$$

where  $\omega$  is the angle between the axes of reference. The equilateral hyperbola through  $(x, y)$  and  $(x_1, y_1)$  is then of the form

$$\frac{\lambda}{\cos \omega} [(X-x_1)\{\cos \omega(X-x) + Y-y\}]$$

$$+ \frac{\mu}{\cos \omega} [(Y-y)\{\cos \omega(Y-y_1) + X-x_1\}]$$

$$+ \nu[(X-x)(Y-y_1) + (X-x_1)(Y-y)] = 0.$$

Hence the equilateral hyperbola through  $(x, y)$ ,  $(x_1, y_1)$ ,  $(x_2, y_2)$ ,  $(x_3, y_3)$  is

$$\begin{vmatrix} \{\cos\omega(X-x)+Y-y\}(X-x_1), & \{\cos\omega(Y-y_1)+X-x_1\}(Y-y), \\ \{\cos\omega(x_2-x)+y_2-y\}(x_2-x_1), & \{\cos\omega(y_2-y_1)+x_2-x_1\}(y_2-y), \\ \{\cos\omega(x_3-x)+y_3-y\}(x_3-x_1), & \{\cos\omega(y_3-y_1)+x_3-x_1\}(y_3-y), \\ (X-x)(Y-y_1)-(X-x_1)(Y-y) & \\ (x_2-x)(y_2-y_1)-(x_2-x_1)(y_2-y) & \\ (x_3-x)(y_3-y_1)-(x_3-x_1)(y_3-y) & \end{vmatrix} = 0.$$

If  $(x, y)$ ,  $(x_1, y_1)$ ,  $(x_2, y_2)$  and  $(x_3, y_3)$  are consecutive points, we have

$$\begin{aligned} x_1 &= x + dx, & y_1 &= y + dy, \\ x_2 &= x + 2dx + d^2x, & y_2 &= y + 2dy + d^2y, \\ x_3 &= x + 3dx + 3d^2x + d^3x, & y_3 &= y + 3dy + 3d^2y + d^3y. \end{aligned}$$

Substituting these values of  $(x_1, y_1)$ ,  $(x_2, y_2)$  and  $(x_3, y_3)$  and simplifying, we get, neglecting higher orders of differentials

$$\begin{vmatrix} (X-x)^2 - (Y-y)^2, & d^2(Y-y) - dy^2(X-x), \\ 2(dx^2 - dy^2), & d^2d^2y - dyd^2x, \\ 6(dx d^2x - dy d^2y), & d^2d^2y - dy d^2x, \\ \cos\omega(Y-y)^2 + (X-x)(Y-y) & \\ 2\cos\omega(dy)^2 + 2dydx & \\ 6\cos\omega dy d^2y + 3dy d^2x + 3d^2d^2y & \end{vmatrix} = 0,$$

as the equation of the osculating equilateral hyperbola at the point  $(x, y)$ . If  $x$  be the independent variable  $d^2x=0$ ,  $d^3x=0, \dots$  and the above reduces to

$$\begin{vmatrix} (X-x)^2 - (Y-y)^2, & Y-y-p(X-x), & \cos\omega(Y-y)^2 + (X-x)(Y-y) & \\ 2(1-p^2), & q, & 2p^2\cos\omega + 2p & \\ -6pq, & r, & 6pq\cos\omega + 3q & \end{vmatrix} = 0,$$

or

$$\begin{aligned} & \{(X-x)^2 - (Y-y)^2\}(2pr-3q^2) - 2(X-x)(Y-y)\{(1-p^2)r+3pq^2\} \\ & + 6\{(Y-y)-p(X-x)\}q(1+p^2) + 2\cos \omega[(X-x)^2 p(pr-3q^2) \\ & - r(Y-y)^2 + 6pq\{Y-y-p(X-x)\}] = 0. \end{aligned}$$

Putting the values of  $p, q, r, s$  from § 1 and simplifying we get for the equation of the osculating equilateral hyperbola

$$\begin{aligned} (X-x)^2 & \begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & f_1 \\ f_{21} & f_{22} & f_2 & 2f_1 \cos \omega - f_2 \\ f_1 & f_2 & 0 & 0 \end{vmatrix} \\ + (Y-y)^2 & \begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & 2f_2 \cos \omega - f_1 \\ f_{21} & f_{22} & f_2 & f_2 \\ f_1 & f_2 & 0 & 0 \end{vmatrix} \\ + 2(X-x)(Y-y) & \begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & f_2 \\ f_{21} & f_{22} & f_2 & f_1 \\ f_1 & f_2 & 0 & 0 \end{vmatrix} \\ - 6J & \begin{vmatrix} Y-y & x-X \\ f_1 & f_2 \end{vmatrix} \begin{vmatrix} 1 & \cos \omega & f_1 \\ \cos \omega & 1 & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} = 0, \end{aligned}$$

or with the notations of § 1

$$P\xi^2 + Q\eta^2 + 2R\xi\eta - 6JS(f_1\xi + f_2\eta) = 0 \quad \dots (1)$$

where  $\xi = X-x$  and  $\eta = Y-y$ .

For centre we have

$$P\xi + R\eta - 3JSf_1 = 0,$$

$$R\xi + Q\eta - 3JSf_2 = 0;$$



whence

$$\frac{\xi}{3JS(f_1Q-f_2R)} = \frac{\eta}{3JS(f_1P-f_2R)} = \frac{1}{PQ-R^2}.$$

Now  $PQ-R^2 = -ST$ ;

$$\therefore \xi = -\frac{3J(f_1Q-f_2R)}{T} = \frac{3JMS}{T},$$

$$\eta = -\frac{3J(f_1P-f_2R)}{T} = -\frac{3JNS}{T};$$

i.e.,

$$\left. \begin{aligned} X &= x + \frac{3JMS}{T}, \\ Y &= y - \frac{3JNS}{T}. \end{aligned} \right\} \quad \dots (2)$$

- 3

The general equation of the osculating conic is <sup>1</sup>

$$\begin{aligned} (3qs-5r^2)\{Y-y-p(X-x)\}^2 + \{(Y-y)r-(X-x)(pr-3q^2)\}^2 \\ = 18q^3\{Y-y-p(X-x)\}. \end{aligned} \quad \dots (3)$$

Now

$$\begin{aligned} 3qs-5r^2 &= \frac{1}{f_1^3} \left\{ 3J \begin{vmatrix} K_1 & K_2 & 5K \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} - 5 \begin{vmatrix} J_1 & J_2 & 3J \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix}^2 \right\} \\ &= \frac{1}{f_1^3} [3J\{-f_2^2K_1 + f_1f_2K_2 + 5K \begin{vmatrix} f_{21} & f_{22} \\ f_1 & f_2 \end{vmatrix} - 5K^2\}] \\ &= \frac{1}{f_1^3} [-3f_2^2J\{3J(f_{12}^2 + f_2f_{112} - f_{11}f_{22} - f_1f_{122}) \end{aligned}$$

<sup>1</sup> Vide—A General Theory of Osculating Conics, *loc. cit.*

$$\begin{aligned}
& +3J_1(f_2f_{12}-f_1f_{22})-2f_1f_2J_1-f_2^2J_{11}+f_{11}f_2J_2+f_1f_{11}J_2 \\
& +f_1f_2J_{12}+3f_1f_2J\{(f_{22}f_{12}+f_2f_{122}-f_{12}f_{22}-f_1f_{222})3J+3J_2(f_2f_{12} \\
& -f_1f_{22})-2f_2f_{22}J_1-f_2^2J_{11}+f_{11}f_2J_2+f_1f_{22}J_2+f_1f_2J_{22}\} \\
& +15J(f_2f_{12}-f_1f_{22})\{3J(f_2f_{12}-f_1f_{22})-f_2^2J_1+f_1f_2J_2\} \\
& -5\{9J^2(f_2f_{12}-f_1f_{22})^2+f_2^2J_1^2+f_1^2f_2^2J_2^2-2f_1f_2^2J_1J_2 \\
& -6f_2^2JJ_1(f_2f_{12}-f_1f_{22})+6f_1f_2JJ_2(f_2f_{12}-f_1f_{22})\}] \\
& = \frac{1}{f_2^5} \left[ -5f_2^2 \begin{vmatrix} J_1 & J_2 \\ f_1 & f_2 \end{vmatrix}^2 - 3f_2^2J \begin{vmatrix} J_{11} & J_{12} & f_1 \\ J_{21} & J_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} \right. \\
& \quad \left. + 12f_2^2J \begin{vmatrix} f_{11} & f_{12} & J_1 \\ f_{21} & f_{22} & J_2 \\ f_1 & f_2 & 0 \end{vmatrix} + 27f_2^2J^2 \begin{vmatrix} f_{11} & f_{12} \\ f_{12} & f_{22} \end{vmatrix} \right]
\end{aligned}$$

Putting

$$L = \frac{5}{3} \begin{vmatrix} J_1 & J_2 \\ f_1 & f_2 \end{vmatrix}^2 + J \begin{vmatrix} J_{11} & J_{12} & f_1 \\ J_{21} & J_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} - 4J \begin{vmatrix} f_{11} & f_{12} & J_1 \\ f_{21} & f_{22} & J_2 \\ f_1 & f_2 & 0 \end{vmatrix} - 9J^2 \begin{vmatrix} f_{11} & f_{12} \\ f_{12} & f_{22} \end{vmatrix}$$

we have

$$3qs-5r^2 = -\frac{3L}{f_2^5}.$$

Also

$$\begin{aligned}
pr-3q^2 &= \frac{f_1}{f_2^3} \begin{vmatrix} J_1 & J_2 & 3J \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} - 3 \frac{J^2}{f_2^3}, \\
&= \frac{1}{f_2^3} \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_1 \\ f_1 & f_2 & 0 \end{vmatrix} \cdot \text{on simplification.}
\end{aligned}$$

Substituting these in (3), the equation transforms into

$$\begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & Y-y \\ f_{21} & f_{22} & f_2 & x-X \\ f_1 & f_2 & 0 & 0 \end{vmatrix} = 3L \begin{vmatrix} Y-y & x-X \\ f_1 & f_2 \end{vmatrix} + 18J^2 \begin{vmatrix} Y-y & x-X \\ f_1 & f_2 \end{vmatrix}$$

which is therefore the equation to the osculating conic at the point  $(x, y)$ .

The co-ordinates of the centre are

$$X = x - \frac{3qr}{3qs - 5r^2},$$

$$Y = y - \frac{3q(pr - 3q^2)}{3qs - 5r^2},$$

which readily transform into

$$\left. \begin{aligned} X = x - \frac{J}{L} \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_1 \\ f_1 & f_2 & 0 \end{vmatrix} &= x - \frac{JM}{L}, \\ Y = y + \frac{J}{L} \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_1 \\ f_1 & f_2 & 0 \end{vmatrix} &= y + \frac{JN}{L}. \end{aligned} \right\} \dots (4)$$

4

The axes of the conic are determined as follows.

Putting  $\xi = X - x$  and  $\eta = Y - y$ , the general equation of the osculating conic may be written as

$$(3qs - 5r^2)(\eta - p\xi)^2 + \{\eta r - (pr - 3q^2)\xi\}^2 - 18q^2(\eta - p\xi) = 0,$$

$$\text{or, } \xi^2\{p^2\lambda + (pr - 3q^2)\} + \eta^2(\lambda + r^2) - 2\xi\eta\{p\lambda + r(pr - 3q^2)\}$$

$$- 18q^2\eta + 18pq^2\xi = 0,$$

where

$$\lambda = 3qs - 5r^2.$$

The axes of the conic

$$ax^2 + 2hxy + by^2 + 2gx + 2fy + c = 0$$

are given by

$$r^4(ab-h^2)^3 - \Delta(ab-h^2)(a+b-2h\cos\omega)r^2 + \Delta^2 = 0$$

where

$$\Delta = \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix},$$

$r$  being a semi-axis of the conic.

$$\text{Now } \frac{\Delta}{ab-h^2} = g\bar{x} + f\bar{y} + c, \quad (\bar{x}, \bar{y}) \text{ being the centre.}$$

Hence in our case

$$\frac{\Delta}{ab-h^2} = -9pq^3 \frac{3qr}{\lambda} + 9q^3 \frac{3q(pr-3q^3)}{\lambda} = -\frac{81q^4}{\lambda};$$

$$\text{and } ab-h^2 = \{p^2\lambda + (pr-3q^3)^2\}(\lambda+r^2) - \{p\lambda + r(pr-3q^3)\}^2 = 9\lambda q^4.$$

Hence if  $r_1$  and  $r_2$  be the semi-axes of the conic

$$\begin{aligned} r_1^2 + r_2^2 &= \frac{\Delta(a+b-2h\cos\omega)}{(ab-h^2)^2} \\ &= -\frac{9q^4}{\lambda^2} \{ \lambda(1+p^2+2p\cos\omega) + (pr-3q^3)^2 + 2r(pr-3q^3)\cos\omega \} \\ &= -\frac{J^2}{L^2} \left\{ 3L \begin{vmatrix} 1 & \cos\omega & f_1 \\ \cos\omega & 1 & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} - \begin{vmatrix} 1 & \cos\omega & M \\ \cos\omega & 1 & N \\ M & N & 0 \end{vmatrix} \right\} \\ &= \frac{J^2}{L^2} (T-3LS); \end{aligned}$$

$$\begin{aligned} r_1^2 r_2^2 &= \frac{\Delta^2}{(ab-h^2)^3} = \left( \frac{\Delta}{ab-h^2} \right)^2 \frac{1}{ab-h^2}, \\ &= -27 \frac{J^4}{L^3}. \end{aligned}$$

The equation to the osculating parabola is<sup>1</sup>

$$\{(X-x)(pr-3q^2)-(Y-y)r\}^2=18q^3\{Y-y-p(X-x)\}$$

which transforms into

$$\begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & Y-y \\ f_{21} & f_{22} & f_2 & x-X \\ f_1 & f_2 & 0 & 0 \end{vmatrix} = 18J^3 \begin{vmatrix} Y-y & x-X \\ f_1 & f_2 \end{vmatrix}.$$

In rectangular co-ordinates, the semi-latus rectum  $l$  is given by

$$l = \frac{27q^3}{\{(pr-3q^2)^2+r^2\}^{\frac{3}{2}}} = \frac{27J^3}{\left[ \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_1 \\ f_1 & f_2 & 0 \end{vmatrix}^2 + \begin{vmatrix} J_1 & J_2 & 3J \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix}^2 \right]^{\frac{3}{2}}} \\ = \frac{27J^3}{[M^2+N^2]^{\frac{3}{2}}}.$$

The directrix of the osculating parabola is

$$r(X-x)+(pr-3q^2)(Y-y)-\frac{3}{2}q(1+p^2)=0,$$

or

$$\begin{vmatrix} J_1 & J_2 & 3J & 0 \\ f_{11} & f_{12} & f_1 & X-x \\ f_{21} & f_{22} & f_2 & Y-y \\ f_1 & f_2 & 0 & 0 \end{vmatrix} + \frac{3}{2}J(f_1^2+f_2^2)=0.$$

The circle of curvature in rectangular co-ordinates is

$$(X-x)^2+(Y-y)^2=\frac{2(1+p^2)}{q}\{Y-y-p(X-x)\},$$

<sup>1</sup> *Vide*—A General Theory of Osculating Conics.

which transformed is

$$(X-x)^2 + (Y-y)^2 = \frac{2(f_1^2 + f_2^2)}{J} \begin{vmatrix} Y-y & x-X \\ f_1 & f_2 \end{vmatrix}.$$

The co-ordinates of the centre of curvature are

$$X = x - \frac{(1+p^2)p}{q} = x + \frac{f_1(f_1^2 + f_2^2)}{J},$$

$$Y = y + \frac{1+p^2}{q} = y + \frac{f_2(f_1^2 + f_2^2)}{J};$$

and the radius of curvature  $\rho$  is given by

$$\rho = \frac{(1+p^2)^{\frac{3}{2}}}{q} = \frac{(f_1^2 + f_2^2)}{J}.$$

# 7

The osculating conic will be an ellipse, hyperbola or parabola according as  $3qs-5r^2$  is positive, negative or zero. But we have seen that  $3qs-5r^2 = -\frac{3L}{f_2^3}$ . Hence the osculating conic will be an ellipse, hyperbola or parabola according as  $L$  is negative, positive or zero. Hence the condition<sup>1</sup> for a parabolic point is  $L=0$ , i.e.,

$$\frac{5}{3} \begin{vmatrix} J_1 & J_2 \\ f_1 & f_2 \end{vmatrix}^2 + J \begin{vmatrix} J_{11} & J_{12} & f_1 \\ J_{21} & J_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix} - 4J \begin{vmatrix} f_{11} & f_{12} & J_1 \\ f_{21} & f_{22} & J_2 \\ f_1 & f_2 & 0 \end{vmatrix} - 9J^2 \begin{vmatrix} f_{11} & f_{12} \\ f_{21} & f_{22} \end{vmatrix} = 0.$$

The condition that the osculating conic may be an equilateral hyperbola is

$$\lambda(1+p^2) + r^2 + (pr-3q^2)^2 = 0,$$

<sup>1</sup> This condition and the condition for a sextactic point given later were communicated to me, without proof by Prof. Harold Hilton to whom I wish to express my gratitude.

which transforms into

$$3L(f_1^2 + f_2^2) = \begin{vmatrix} J_1 & J_2 & 3J \\ f_{11} & f_{12} & f_1 \\ f_1 & f_2 & 0 \end{vmatrix} + \begin{vmatrix} J_1 & J_2 & 3J \\ f_{21} & f_{22} & f_2 \\ f_1 & f_2 & 0 \end{vmatrix},$$

or 
$$3L(f_1^2 + f_2^2) = M^2 + N^2.$$

8

The condition that the osculating conic may have a six-pointic contact at  $(x, y)$  is <sup>1</sup>

$$40r^3 - 45qrs + 9q^2t = 0,$$

or 
$$3q \frac{d}{dx} (3qs - 5r^2) - 8(3qs - 5r^2) \frac{dq}{dx} = 0,$$

or 
$$3J \frac{d}{dx} (L) - 8L \frac{d}{dx} (J) = 0,$$

or 
$$3J \left( L_1 - \frac{f_1}{f_2} L_2 \right) - 8L \left( J_1 - \frac{f_1}{f_2} J_2 \right) = 0,$$

where 
$$L_1 = \frac{\partial L}{\partial x} \text{ and } L_2 = \frac{\partial L}{\partial y};$$

or 
$$3J \begin{vmatrix} L_1 & L_2 \\ f_1 & f_2 \end{vmatrix} - 8L \begin{vmatrix} J_1 & J_2 \\ f_1 & f_2 \end{vmatrix} = 0.$$

My best thanks are due to Prof. S. Mukhopadhyaya for suggestions and encouragement and for the help received from his published works.

<sup>1</sup> *Vide*—A General Theory of Osculating Conics.

# CERTAIN PRODUCTS INVOLVING THE DIVISORS OF NUMBERS

By

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(Communicated by Dr. B. Datta)

The products of this note, originating in a generalized Lambert series, are sufficiently curious to deserve a passing notice. By expanding these products for special choices of the arbitrary numerical function  $f(n)$  occurring in the exponents of the several factors, it is possible to obtain numerous theorems on partitions of integers. The most of these appear to be too complicated to be of much interest, although some of them have already been obtained otherwise by various writers and have appeared in the literature. A few, however, might prove worth developing.

§1. Let  $m, n$  denote integers  $>0$ , of which  $m$  is odd and  $n$  arbitrary. If either of  $m$  or  $n$  occurs under  $\Sigma$  or  $\Pi$ , the sum or product is with respect to all values of the  $m$  or  $n$  as defined. The function  $f(y)$  is numerical; that is, for each integer value  $>0$  of  $y$ ,  $f(y)$  takes a single finite value. We shall write

$$f'(n) \equiv f(1) + f(d_1) + f(d_2) + \dots + f(n),$$

where  $1, d_1, d_2, \dots, n$  are all the divisors of  $n$ , and it is assumed that for some  $|x| > 0$  the series

$$\Sigma f'(n)x^n, = \Sigma \frac{f(n)x^n}{1-x^n} \quad \dots \quad (A)$$

is absolutely convergent. When for a specific  $f$  the convergence condition is  $|x| < k$ , and the variable  $x$  is replaced by  $g(y)$ , it is further assumed that the condition is transformed, in accordance with the substitution, into  $|y| < k'$ .



§2. Dividing (A) throughout by  $x$  and integrating between the limits 0,  $x$ , we get, on taking exponentials of both sides,

$$\Pi(1-x^n)^{f(n)/n} = e^{-\sum f(n)x^n/n} \quad \dots (1)$$

§3. Let  $\mu(n)$  as usual denote the function of Möbius;  $\mu(n)=0$  if  $n$  is divisible by any square  $>1$ , and otherwise  $\mu(n)=+1$  or  $-1$  according as  $n$  is the product of an even or an odd number of distinct primes. By convention  $\mu(1)=1$ . The relation between  $f$ ,  $f'$  can be reversed, giving

$$f(n) = \sum \mu(d)f'(\delta),$$

where the  $\sum$  refers to all pairs  $(d, \delta)$  of divisors such that  $d\delta=n$ .

If now we define  $f''(n)$  by

$$f''(n) = \sum \mu(d)f(\delta),$$

it follows from (1) by a change in notation that

$$\Pi(1-x^n)^{f''(n)/n} = e^{-\sum f(n)x^n/n} \quad \dots (2)$$

The formulas (1), (2) are merely different expressions of one fact; when the function occurring in the exponents under  $\Pi$  is given, we use (1), otherwise (2).

§4. When only plus signs occur in the products we need a theorem stated by Liouville,

$$f_1(m) = -f'(m), \quad f_1(2n) = 2f'(n) - f'(2n),$$

where the definition of  $f_1(n)$  is

$$f_1(n) = \sum (-1)^\delta f(d),$$

the  $\sum$  extending as before to all pairs  $(d, \delta)$  of conjugate divisors of  $n$ .

To prove this, assume that for some  $s$  the Dirichlet series

$$\sum \frac{(-1)^s}{n^s}, \quad \sum \frac{f(n)}{n^s},$$

are both absolutely convergent. On multiplying these together and using the identity

$$1 + \frac{1}{3^s} + \frac{1}{5^s} + \dots = \left(1 - \frac{1}{2^s}\right) \left(1 + \frac{1}{2^s} + \frac{1}{3^s} + \dots\right),$$

we note that the coefficient of  $\frac{1}{n^s}$ , which evidently is  $f_1(n)$ , is as stated by the theorem.

Proceeding as in §2 we get

$$\Pi(1+x^n)^{f(n)/n} = e^{-\sum f_1(n)x^n/n} \quad \dots (3)$$

§5. When only odd integers  $n$  occur in the product we require  $f_2(n)$ , defined by

$$f_2(n) = \sum f(t),$$

the  $\sum$  extending to all odd divisors  $t$  of  $n$ . Then

$$\sum \frac{f(n)x^n}{1-x^n} = \sum f_2(n)x^n,$$

and as before we infer

$$\Pi(1-x^n)^{f(n)/n} = e^{-\sum f_2(n)x^n/x^n} \quad \dots (4)$$

§6. Obviously (3) can be obtained from (1) by changing  $x$  into  $x^s$  and dividing the resulting identity member by member by (1).

The result of changing  $x$  into  $-x$  in (4) is

$$\Pi(1+x^n)^{f(n)/n} = e^{-\sum f_2(2n)x^{2n}/2n} \cdot e^{\sum f'(n)x^n/n}. \quad \dots (5)$$

Hence by division we get from (4), (5),

$$\Pi\left(\frac{1-x^n}{1+x^n}\right)^{f(n)/n} = e^{-\sum f'(n)x^n/n}. \quad \dots (6)$$

§7. As the simplest illustrations of (1)-(6) we may take  $f(n)=n$  for all integers  $n$ . Then  $f'(n)=\sigma(n)$ , the sum of the divisors of  $n$ , and (1) becomes

$$\Pi(1-x^n) = e^{-\sum \sigma(n)x^n/n}, \quad \dots (1.1)$$

which is merely a restatement, in its simplest reading, of a well-known relation between partitions and divisors. For this choice of  $f$  the rest can be interpreted in similar ways.

For the choice  $f(n)=1$  or 0 according as  $n$  is or is not the integer  $r > 0$ , (2) gives

$$\Pi(1-x^{r \cdot n})^{\mu(n)/n} = e^{-x^r}, \quad \dots \quad (2.1)$$

and hence, for  $r=1$ ,

$$\Pi(1-x^n)^{\mu(n)/n} = e^{-x}. \quad \dots \quad (2.12)$$

In all such examples convergence conditions upon  $x$  can be readily determined from the corresponding series as indicated in §2.

If  $f(n) \equiv \lambda(n) = +1$  or  $-1$  according as the *total* number of prime divisors of  $n$  is even or odd, we have  $f'(n)=1$  or 0 according as  $n$  is or is not a square. Hence (1) gives

$$\Pi(1-x^n)^{\lambda(n)/n} = e^{-\sum x^{n^2}/n^2}. \quad \dots \quad (1.2)$$

For the choice  $f(n)=1$ , we get identities involving the number  $v(n)$  of divisors of  $n$ ;  $f'(n)$  in this case reduces to 1 for  $n=1$ , to zero for  $n > 1$ , providing a check.

Identities concerning partitions into primes exclusively (or into any other class of numbers, by the appropriate choice of  $f$ ), can be obtained by expanding the exponential function and developing the product, as in

$$\Pi' \frac{1}{1-x^p} = e^{\sum \hat{\omega}(n) x^n / n} \quad \dots \quad (1.3)$$

where  $\hat{\omega}(n)$  is the sum of the distinct prime divisors  $\leq 1$  of  $n$ , and  $\Pi'$  refers to all primes  $p \leq 1$ .

As a last example take  $f(n) = \phi_r(n)$ , where  $\phi_r(n)$  is Jordan's totient of order  $r$ ;  $\phi_r(n)$  the number of sets of  $r$  equal or distinct integers equal to or less than  $n$  and coprime with  $n$ . Then  $\phi_1(n) = \phi(n)$ , Euler's function. It is well-known that  $\sum \phi_r(d) = n^r$ . Let  $\theta$  denote the operation  $x \frac{d}{dx}$ , viz., the  $x$ -derivative of the operand is to be multiplied by  $x$ , and  $\theta^r$  means  $\theta$  operating upon the result of  $\theta^{r-1}$ . Then if  $\theta^0 = 1$ ,

$$\sum n^r x^n = \theta^r \sum x^n = \theta^r \left( \frac{x}{1-x} \right) \equiv F_r(x),$$

and from (1) we get

$$\prod (1-x^n)^{\phi_r(n)/n} = e^{-F_{r-1}(x)} \quad (r \geq 1). \quad \dots \quad (1.4)$$

For example taking  $r=1$ ,  $x=\frac{1}{2}$ ,

$$\prod \left(1 - \frac{1}{2^n}\right)^{\phi(n)/n} = \frac{1}{e}; \quad \dots \quad (1.41)$$

for  $r=2$ ,  $x=\frac{1}{2}$

$$\prod \left(1 - \frac{1}{2^n}\right)^{\phi_2(n)/n} = \frac{1}{e^2}; \quad \dots \quad (1.42)$$

for  $r=3$ ,  $x=\frac{1}{2}$ ,

$$\prod \left(1 - \frac{1}{2^n}\right)^{\phi_3(n)/n} = \frac{1}{e^3};$$

and so on.

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# ON LIQUID MOTION INSIDE CERTAIN ROTATING CIRCULAR ARCS

BY

SUDDHODAN GHOSE.

In the present paper, I have discussed the problem of liquid motion in rotating vessels when the boundary consists of (1) four orthogonal circles, (2) three circles, one cutting the other two orthogonally (3) two orthogonal circles. I have also deduced some particular cases of boundaries consisting of arcs of circles and straight lines.

1. Let 
$$x+iy=c \tan \frac{1}{2}(\xi+i\eta)$$

so that  $\xi=\text{const}$  and  $\eta=\text{const}$  represent two systems of co-axial circles cutting orthogonally.

If  $\psi$  be the stream function, and  $\omega$  the angular velocity of the cylinder, then we have

$$\frac{\partial^2 \psi}{\partial \xi^2} + \frac{\partial^2 \psi}{\partial \eta^2} = 0$$

at all points in the liquid and

$$\psi = \frac{1}{2} \omega (x^2 + y^2) + \text{const}$$

at all points on the boundary.

Evidently,

$$y = c + 2c \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \cos n\xi,$$

$$x = 2c \sum_{n=1}^{\infty} (-1)^{n+1} e^{-n\eta} \sin n\xi.$$

On the boundary  $\xi = \text{const}$ ,

$$\psi = -c\omega \cot \xi + \text{const}$$

$$= 2c^2 \omega \cot \xi \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \sin n\xi + \text{const.}$$

On the boundary  $\eta = \text{const.}$

$$\psi = c\omega y \coth \eta + \text{const.}$$

$$= 2c^2 \omega \coth \eta \sum_{1}^{\infty} (-1)^n e^{-n\eta} \cos n\xi + \text{const.}$$

*Rectangle bounded by four circular arcs*

2. Let the section of the cylinder be bounded by the circles

$$\xi = a_1, \xi = a_2, \eta = \beta_1 \text{ and } \eta = \beta_2.$$

Assume

$$\begin{aligned} \psi = & 2c^2 \omega \sum_{1}^{\infty} (-1)^n \frac{e^{-n\beta_2} \coth \beta_2 \sinh n(\eta - \beta_1) + e^{-n\beta_1} \coth \beta_1 \sinh n(\beta_2 - \eta)}{\sinh n(\beta_2 - \beta_1)} \\ & \times \cos n\xi \\ & + 2c^2 \omega \sum_{1}^{\infty} (-1)^n \frac{\sin n a_2 \cot a_2 \sin n(\xi - a_1) + \sin n a_1 \cot a_1 \sin n(a_2 - \xi)}{\sin n(a_2 - a_1)} e^{-n\eta} \\ & + \sum_{m=0}^{\infty} \left\{ P_m \sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - a_1) \right. \\ & \left. + Q_m \sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - a_2) \right\} \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta - \delta) \\ & + \sum_{m=0}^{\infty} \left\{ R_m \sinh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \beta_1) \right. \\ & \left. + S_m \sinh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \beta_2) \right\} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma) \quad \dots \quad (1) \end{aligned}$$

where

$$\begin{aligned} 2\epsilon_1 &= a_2 - a_1 & 2\gamma &= a_2 + a_1 \\ 2\epsilon_2 &= \beta_2 - \beta_1, & 2\delta &= \beta_2 + \beta_1, \quad \dots \quad (2) \end{aligned}$$

When  $\xi = a_1$  and  $\beta_1 \leq \eta \leq \beta_s$ , we have

$$\begin{aligned}
 & 2c^2\omega \cot a_1 \sum_{1}^{\infty} (-1)^s e^{-s\eta} \sin na_1 \\
 &= 2c^2\omega \cot a_1 \sum_{1}^{\infty} (-1)^s e^{-s\eta} \sin na_1 \\
 &+ 2c^2\omega \sum_{1}^{\infty} (-1)^s \frac{(e^{-n\beta_s} \coth \beta_s - e^{-n\beta_1} \coth \beta_1) \cosh n\epsilon_s \sinh n(\eta - \delta) + (e^{-n\beta_s} \coth \beta_s + e^{-n\beta_1} \coth \beta_1) \sinh n\epsilon_s \cosh n(\eta - \delta) \cos na_1}{\sinh 2n\epsilon_s} \\
 &- \sum_{n=0}^{\infty} Q_n \sinh \frac{(2m+1)\pi\epsilon_1}{\epsilon_s} \cos \frac{(2m+1)\pi}{2\epsilon_s} (\eta - \delta).
 \end{aligned}$$

Multiplying both sides by  $\cos \frac{(2m+1)\pi}{2\epsilon_s} (\eta - \delta)$  and integrating between  $\beta_1$  and  $\beta_s$  and simplifying we have

$$Q_n = \frac{4c^2\omega}{\sinh \frac{(2m+1)\pi\epsilon_1}{\epsilon_s}} \sum_{n=1}^{\infty} (-1)^{m+n} \cdot \frac{(2m+1)\pi}{(2m+1)^2\pi^2 + 4n^2\epsilon_s^2} \cdot (e^{-n\beta_s} \coth \beta_s + e^{-n\beta_1} \coth \beta_1) \cos na_1. \quad (3)$$

Putting  $\xi = a_s$  and proceeding in the same way as above we have

$$P_m = \frac{4c^2\omega}{\sinh \frac{(2m+1)\pi\epsilon_1}{\epsilon_s}} \sum_{n=1}^{\infty} (-1)^{m+s+1} \cdot \frac{(2m+1)\pi}{(2m+1)^2\pi^2 + 4n^2\epsilon_s^2} \cdot (e^{-n\beta_s} \coth \beta_s + e^{-n\beta_1} \coth \beta_1) \cos na_s. \quad (4)$$



From the boundary condition on  $\eta = \beta_1$ , we have, by multiplying both sides by  $\cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma) d\xi$  and integrating between  $a_1$  and  $a_s$ ,

$$S_m = \frac{4c^2\omega}{\sinh \frac{(2m+1)\pi\epsilon_s}{\epsilon_1}} \sum_{n=1}^{\infty} (-1)^{m+n} \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon_s^2} (\sin na_s \cot a_s + \sin na_1 \cot a_1) e^{-n\beta_1}. \quad \dots \quad (5)$$

Similarly putting  $\eta = \beta_s$  and proceeding as above we have

$$R_m = \frac{4c^2\omega}{\sinh \frac{(2m+1)\pi\epsilon_s}{\epsilon_1}} \sum_{n=1}^{\infty} (-1)^{m+n+1} \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon_s^2} (\sin na_s \cot a_s + \sin na_1 \cot a_1) e^{-n\beta_s}. \quad \dots \quad (6)$$

Thus  $\psi$  is completely determined.

$$\begin{aligned} \therefore \phi = & 2c^2\omega \sum_{\frac{1}{1}}^{\infty} (-1)^n \frac{e^{-n\beta_s} \coth \beta_s \cosh n(\eta - \beta_1) - e^{-n\beta_1} \coth \beta_1 \cosh n(\beta_s - \eta)}{\sinh n(\beta_s - \beta_1)} \sin n\xi \\ & + 2c^2\omega \sum_{\frac{1}{1}}^{\infty} (-1)^n \frac{\sin na_s \cot a_s \cos n(\xi - a_1) - \sin na_1 \cot a_1 \cos n(a_s - \xi)}{\sin n(a_s - a_1)} e^{-n\eta} \\ & - \sum_{m=0}^{\infty} \left\{ P_m \cosh \frac{(2m+1)\pi}{2\epsilon_s} (\xi - a_1) + Q_m \cosh \frac{(2m+1)\pi}{2\epsilon_s} (\xi - a_s) \right\} \sin \frac{(2m+1)\pi}{2\epsilon_s} (n - \delta) \\ & + \sum_{m=0}^{\infty} \left\{ R_m \cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \beta_1) + S_m \cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \beta_s) \right\} \sin \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma). \quad \dots \quad (7) \end{aligned}$$

$$\begin{aligned}
 \text{If we put} \quad \psi_1 = & \sum_{m=0}^{\infty} \left\{ P_m \sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - \alpha_1) + Q_m \sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - \alpha_2) \right\} \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta - \delta) \\
 & + \sum_{m=0}^{\infty} \left\{ R_m \sinh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \beta_1) + S_m \sinh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \beta_2) \right\} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma); \quad \dots \quad (8)
 \end{aligned}$$

then the part  $\psi_1$  of  $\psi$  can be proved to be

$$\begin{aligned}
 &= 2c^2 \omega \sum_{m=0}^{\infty} (-1)^m \left[ \frac{\sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - \gamma)}{\sinh \frac{(2m+1)\pi \epsilon_1}{2\epsilon_2}} \sum_{n=1}^{\infty} (-1)^n \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 + 4n^2 \epsilon_2^2} A_n \right. \\
 &\quad + \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - \gamma)}{\cosh \frac{(2m+1)\pi \epsilon_1}{2\epsilon_2}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 + 4n^2 \epsilon_2^2} B_n \left. \right] \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta - \delta) \\
 &+ 2c^2 \omega \sum_{m=0}^{\infty} (-1)^m \left[ \frac{\sin \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \delta)}{\sinh \frac{(2m+1)\pi \epsilon_2}{2\epsilon_1}} \sum_{n=1}^{\infty} (-1)^n \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 - 4n^2 \epsilon_1^2} C_n \right. \\
 &\quad + \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \delta)}{\cosh \frac{(2m+1)\pi \epsilon_2}{2\epsilon_1}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 - 4n^2 \epsilon_1^2} D_n \left. \right] \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma)
 \end{aligned}$$

when

$$A_n = (e^{-n\beta_2} \coth \beta_2 + e^{-n\beta_1} \coth \beta_1)(\cos na_1 - \cos na_2)$$

$$B_n = (e^{-n\beta_2} \coth \beta_2 + e^{-n\beta_1} \coth \beta_1)(\cos na_1 + \cos na_2)$$

$$C_n = (\sin na_2 \cot a_2 + \sin na_1 \cot a_1)(e^{-n\beta_1} e^{-n\beta_2})$$

$$D_n = (\sin na_2 \cot a_2 + \sin na_1 \cot a_1)(e^{-n\beta_1} + e^{-n\beta_2})$$

...

$$\therefore \psi_1 = 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \left[ A_n \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 + 4n^2 \epsilon^2} \cdot \frac{\sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - \gamma)}{\sinh \frac{(2m+1)\pi \epsilon_1}{2\epsilon_2}} \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta - \delta) \right]$$

$$+ C_n \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 - 4n^2 \epsilon^2} \cdot \frac{\sinh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \delta)}{\sinh \frac{(2m+1)\pi \epsilon_2}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma) \Big]$$

$$- 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \left[ B_n \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 + 4n^2 \epsilon^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_2} (\xi - \gamma)}{\cosh \frac{(2m+1)\pi \epsilon_1}{2\epsilon_2}} \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta - \delta) \right]$$

$$+ D_n \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2 \pi^2 - 4n^2 \epsilon^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta - \delta)}{\cosh \frac{(2m+1)\pi \epsilon_2}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi - \gamma) \Big]$$

$$\text{Let } u = \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} \left\{ \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_s} (\xi-\gamma)}{\cosh \frac{(2m+1)\pi\epsilon_1}{2\epsilon_s}} \cos \frac{(2m+1)\pi}{2\epsilon_s} (\eta-\delta) + \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta)}{\cosh \frac{(2m+1)\pi\epsilon_s}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma) \right\}. \quad (10)$$

$$\text{When } \xi = \alpha_1 \text{ or } \alpha_s \text{ and } \beta_2 \geq \eta \geq \beta_1, \quad u = \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} \cos \frac{(2m+1)\pi}{2\epsilon_s} (\eta-\delta) = \frac{\pi}{4}.$$

$$\text{Similarly when } \eta = \beta_1 \text{ or } \beta_s \text{ and } \alpha_2 \geq \xi \geq \alpha_1 \quad u = \frac{\pi}{4}.$$

$$\text{Also } \frac{\partial^2 u}{\partial \xi^2} + \frac{\partial^2 u}{\partial \eta^2} = 0 \quad \therefore u = \frac{\pi}{4} \text{ within the boundaries.}$$

$$\text{Since } \frac{\partial^2 u}{\partial \xi^2} = -\frac{\partial^2 u}{\partial \eta^2} \quad \therefore \left( \frac{\partial^2}{\partial \xi^2} + n^2 \right)^{-1} u = \left( -\frac{\partial^2}{\partial \eta^2} + n^2 \right)^{-1} u$$

Performing these operations on both sides of  $u$  we have

$$\frac{\pi}{4n^2} = \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} \left\{ \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_s} (\xi-\gamma)}{\cosh \frac{(2m+1)\pi\epsilon_1}{2\epsilon_s}} \cdot \frac{\cos \frac{(2m+1)\pi}{2\epsilon_s} (\eta-\delta)}{\frac{(2m+1)^2 \pi^2}{4\epsilon_s^2} + n^2} - \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta)}{\cosh \frac{(2m+1)\pi\epsilon_s}{2\epsilon_1}} \cdot \frac{\cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma)}{\frac{(2m+1)^2 \pi^2}{4\epsilon_1^2} - n^2} \right\} + f_1(\eta) \cos n(\xi-\gamma)$$

$$= \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} \left\{ \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_2} (\xi-\gamma)}{\cosh \frac{(2m+1)\pi\epsilon_1}{2\epsilon_2}} \cdot \frac{\cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta-\delta)}{\frac{(2m+1)^2\pi^2}{4\epsilon_2^2} + n^2} \right.$$

$$\left. - \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta)}{\cosh \frac{(2m+1)\pi\epsilon_2}{2\epsilon_1}} \cdot \frac{\cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma)}{\frac{(2m+1)^2\pi^2}{2\epsilon_1^2} - n^2} \right\} + f_2(\xi) \cosh n(\eta-\delta)$$

where  $a_2 > \xi > a_1$  and  $\beta_2 > \eta > \beta_1$   $\therefore f_2(\xi) = c \cos n(\xi-\gamma)$  and  $f_1(\eta) = c \cosh n(\eta-\delta)$ .

Putting  $\xi = a_2$  and  $\eta = \beta_2$  we have

$$C = \frac{\pi}{4n^2 \cos n\epsilon_1 \cosh n\epsilon_2}.$$

$$\therefore \frac{\pi}{4} \left[ 1 - \frac{\cos n(\xi-\gamma) \cosh n(\eta-\delta)}{\cos n\epsilon_1 \cosh n\epsilon_2} \right] = \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} \left\{ \frac{4n^2\epsilon_2^2}{(2m+1)^2\pi^2 + 4n^2\epsilon_2^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_2} (\xi-\gamma)}{\cosh \frac{(2m+1)\pi\epsilon_1}{2\epsilon_2}} \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta-\delta) \right. \\ \left. - \frac{4n^2\epsilon_1^2}{(2m+1)^2\pi^2 - 4n^2\epsilon_1^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta)}{\cosh \frac{(2m+1)\pi\epsilon_2}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma) \right\}. \quad \dots \quad (11)$$

Subtracting (11) from (10) and dividing by  $\pi$  we have

$$\begin{aligned}
 \frac{\cos n(\xi-\gamma) \cosh n(\eta-\delta)}{4 \cos n\epsilon_1 \cosh n\epsilon_2} &= \sum_{m=0}^{\infty} (-1)^m \left\{ \frac{(2m+1)\pi}{(2m+1)^2\pi^2 + 4n^2\epsilon_2^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_2} (\xi-\gamma)}{\cosh \frac{(2m+1)\pi\epsilon_1}{2\epsilon_2}} \cos \frac{(2m+1)\pi}{2\epsilon_2} (\eta-\delta) \right. \\
 &\quad \left. + \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon_1^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta)}{\cosh \frac{(2m+1)\pi\epsilon_2}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma) \right\}. \quad \dots (12) \\
 \therefore \psi_1 = 2c^3\omega \sum_{n=1}^{\infty} (-1)^n \left[ A_n \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2\pi^2 + 4n^2\epsilon_2^2} \cdot \frac{\sinh \frac{(2m+1)\pi}{2\epsilon_2} (\xi-\gamma)}{\sinh \frac{(2m+1)\pi\epsilon_1}{2\epsilon_2}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta) \right. \\
 &\quad \left. + C_n \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon_1^2} \cdot \frac{\sinh \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma)}{\sinh \frac{(2m+1)\pi\epsilon_2}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma) \right] \\
 -\frac{1}{2} c^3\omega \sum_{n=1}^{\infty} (-1)^n B_n \frac{\cos n(\xi-\gamma) \cosh n(\eta-\delta)}{\cos n\epsilon_1 \cosh n\epsilon_2} \\
 -2c^3\omega \sum_{n=1}^{\infty} (-1)^n (B_n - D_n) \sum_{m=0}^{\infty} (-1)^m \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon_1^2} \cdot \frac{\cosh \frac{(2m+1)\pi}{2\epsilon_1} (\eta-\delta)}{\cosh \frac{(2m+1)\pi\epsilon_2}{2\epsilon_1}} \cos \frac{(2m+1)\pi}{2\epsilon_1} (\xi-\gamma). \quad \dots (13)
 \end{aligned}$$

Another expression for  $\psi$  can be obtained by assuming

$$\begin{aligned} \psi = & 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \frac{e^{-n\beta_2} \coth \beta_2 \sinh n(\eta - \beta_1) + e^{-n\beta_1} \coth \beta_1 \sinh n(\beta_2 - \eta)}{\sinh n(\beta_2 - \beta_1)} \cos n\xi \\ & + 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin na_2 \cot a_2 \sin n(\xi - a_1) + \sin na_1 \cot a_1 \sin n(a_2 - \xi)}{\sin n(a_2 - a_1)} e^{-n\eta} \\ & + \sum_{n=1}^{\infty} \left\{ P_n \sinh \frac{n\pi}{\epsilon_2} (\xi - a_1) + Q_n \sinh \frac{n\pi}{\epsilon_2} (\xi - a_2) \right\} \sin \frac{n\pi}{\epsilon_2} (\eta - \delta) \\ & + \sum_{n=1}^{\infty} \left\{ R_n \sinh \frac{n\pi}{\epsilon_1} (\eta - \beta_1) + S_n \sinh \frac{n\pi}{\epsilon_1} (\eta - \beta_2) \right\} \sin \frac{n\pi}{\epsilon_1} (\xi - \gamma). \end{aligned}$$

It will be found that

$$\begin{aligned} P_n &= \frac{2c^2 \omega}{\sinh \frac{\epsilon_2}{2m\pi\epsilon_1}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{n\pi}{m^2 \pi^2 + n^2 \epsilon_2^2} (e^{-n\beta_2} \coth \beta_2 - e^{-n\beta_1} \coth \beta_1) \cos na_2 \\ Q_n &= \frac{2c^2 \omega}{\sinh \frac{\epsilon_2}{2m\pi\epsilon_1}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{n\pi}{m^2 \pi^2 + n^2 \epsilon_2^2} (e^{-n\beta_2} \coth \beta_2 - e^{-n\beta_1} \coth \beta_1) \cos na_1 \\ R_n &= \frac{2c^2 \omega}{\sinh \frac{\epsilon_1}{2m\pi\epsilon_2}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{n\pi}{m^2 \pi^2 - n^2 \epsilon_1^2} (\sin na_2 \cot a_2 - \sin na_1 \cot a_1) e^{-n\beta_2} \\ S_n &= \frac{2c^2 \omega}{\sinh \frac{\epsilon_1}{2m\pi\epsilon_2}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{n\pi}{m^2 \pi^2 - n^2 \epsilon_1^2} (\sin na_2 \cot a_2 - \sin na_1 \cot a_1) e^{-n\beta_1} \end{aligned}$$

*Triangle bounded by three circles*

3. Let the cylinder be bounded by  $\xi = a_1$ ,  $\xi = a_2$  and  $\eta = \beta$ .

At the point where  $\xi = a_1$  and  $\xi = a_2$  intersect, we have  $\eta = \infty$ .

Assume

$$\begin{aligned} \psi = & 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \coth \beta e^{-n\eta} \cos n\xi \\ & + 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin na_2 \cot a_2 \sin n(\xi - a_1) + \sin na_1 \cot a_1 \sin n(a_2 - \xi)}{\sin n(a_2 - a_1)} e^{-n\eta} \\ & + c^2 \omega \sum_{m=0}^{\infty} P_m \cos \frac{(2m+1)\pi}{2\epsilon} (\xi - \gamma) e^{-\frac{(2m+1)\pi}{2\epsilon} (\eta - \beta)} \\ & + c^2 \omega \sum_{n=1}^{\infty} \left\{ R_n \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \frac{\sinh a(\xi - a_1)}{\sinh 2a\epsilon} \sin a\lambda \sin a(\eta - \beta) da \right. \\ & \left. + S_n \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \frac{\sinh a(\xi - a_2)}{\sinh 2a\epsilon} \sin a\lambda \sin a(\eta - \beta) da \right\}, \quad \dots \quad (1) \end{aligned}$$

where  $2\gamma = a_2 + a_1$ ,  $2\epsilon = a_2 - a_1$ ; ... (2)

and the form of  $a$  is such that  $a(\eta - \beta)$  is a multiple of  $\pi$  when  $\eta = \infty$

when  $\eta = \infty$  we have  $\psi = 0$

when  $\eta = \beta$  and  $a_2 \geq \xi \geq a_1$

$$\begin{aligned} 2c^2 \omega \coth \beta \sum_{n=1}^{\infty} (-1)^n e^{-n\beta} \cos n\xi = & 2c^2 \omega \coth \beta \sum_{n=1}^{\infty} (-1)^n e^{-n\beta} \cos n\xi \\ & + 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin na_2 \cot a_2 \sin n(\xi - a_1) + \sin na_1 \cot a_1 \sin n(a_2 - \xi)}{\sin n(a_2 - a_1)} e^{-n\beta} \\ & + c^2 \omega \sum_{m=0}^{\infty} P_m \cos \frac{(2m+1)\pi}{2\epsilon} (\xi - \gamma). \end{aligned}$$

Multiplying both sides by

$$\cos \frac{(2m+1)\pi}{2\epsilon} (\xi - \gamma) d\xi$$



and integrating between the limits  $\alpha_1$  and  $\alpha_2$  we have

$$P_n = \sum_{n=1}^{\infty} (-1)^{m+n+1} \frac{4(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon^2} (\sin n\alpha_2 \cot \alpha_2 + \sin n\alpha_1 \cot \alpha_1) e^{-n\beta} \quad (3)$$

when  $\xi = \alpha_1$  and  $\eta$  lies between  $\beta$  and  $\infty$

$$\begin{aligned} 2c^2\omega \cot \alpha_1 & \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \sin n\alpha_1 \\ & = 2c^2\omega \cot \alpha_1 \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \sin n\alpha_1 \\ & + 2c^2\omega \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \coth \beta \cos n\alpha_1 \\ & - c^2\omega \sum_{n=1}^{\infty} S_n \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \sin a\lambda \sin a(\eta-\beta) da. \end{aligned}$$

But for positive values of  $\eta - \beta$

$$\int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \sin a\lambda \sin a(\eta-\beta) da = \frac{\pi}{2} e^{-n(\eta-\beta)}$$

$$\therefore \text{ we have } S_n = (-1)^n \frac{1}{\pi} e^{-n\beta} \coth \beta \cos n\alpha_1. \quad \dots (4)$$

Similarly we have, from condition on the boundary  $\xi = \alpha_2$

$$R_n = (-1)^{n+1} \frac{1}{\pi} e^{-n\beta} \coth \beta \cos n\alpha_2. \quad \dots (5)$$

To evaluate the integrals

$$\begin{aligned} I_1 &= \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \frac{\sinh a(\xi - \alpha_1)}{\sinh 2a\epsilon} \sin a\lambda \sin a(\eta - \beta) da \\ &= \frac{1}{2} \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \frac{\sinh a(\xi - \alpha_1)}{\sinh 2a\epsilon} \{ \cos a(\lambda - \eta + \beta) - \cos a(\lambda + \eta - \beta) \} da \end{aligned}$$

But we have <sup>1</sup>

$$\int_0^\infty \frac{\sinh px}{\sinh qx} \cos rxdx = \frac{\pi}{2q} \cdot \frac{\sin \frac{p\pi}{q}}{\cos \frac{p\pi}{q} + \cosh \frac{r\pi}{q}}, \quad \text{if } p^2 < q^2$$

$$\therefore I_1 = \frac{1}{2} \int_0^\infty e^{-n\lambda} d\lambda \left[ \frac{\pi}{2\epsilon} \cdot \frac{\sin \frac{\pi}{2\epsilon} (\xi - a_1)}{\cos \frac{\pi}{2\epsilon} (\xi - a_1) + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)} \right. \\ \left. - \frac{\pi}{2\epsilon} \cdot \frac{\sin \frac{\pi}{2\epsilon} (\xi - a_1)}{\cos \frac{\pi}{2\epsilon} (\xi - a_1) + \cosh \frac{\pi}{2\epsilon} (\lambda + \eta - \beta)} \right] \\ \frac{\sin \frac{\pi}{2\epsilon} (\xi - a_1)}{\cos \frac{\pi}{2\epsilon} (\xi - a_1) + \cosh \frac{\pi}{2\epsilon} (\lambda + \eta - \beta)} = \frac{\sin \theta_1}{\cos \theta_1 + \cosh v}$$

where

$$\theta_1 = \frac{\pi}{2\epsilon} (\xi - a_1) \text{ and } v = \frac{\pi}{2\epsilon} (\lambda + \eta - \beta).$$

Since  $\lambda$  lies between 0 and  $\infty$  and  $\eta - \beta$  is positive therefore  $v$  is positive. Now,

$$\frac{\sin \theta_1}{\cos \theta_1 + \cosh v} = 2e^{-\lambda} \sin \theta_1 [1 + \sum A_n e^{-nv}]$$

where

$$A_n = (-1)^n [e^{n\theta_1} + e^{-n\theta_1} + e^{(n-2)\theta_1} + e^{-(n-2)\theta_1} + \dots] \\ = (-1)^n 2 [\cos n\theta_1 + \cos (n-2)\theta_1 + \dots] \\ A_n \sin \theta_1 = (-1)^n 2 \sin \theta_1 [\cos n\theta_1 + \cos (n-2)\theta_1 + \dots] \\ = (-1)^n \sin (n+1)\theta_1 \\ \therefore \frac{\sin \theta_1}{\cos \theta_1 + \cosh v} = 2 \sum_{n=1}^{\infty} (-1)^{n+1} e^{-n\lambda} \sin n\theta_1$$

<sup>1</sup> Bierens de Haan, Tables of Def. Int. (7) 265.

$$\begin{aligned}
& \therefore \int_0^{\infty} \frac{\sin \frac{\pi}{2\epsilon} (\xi - a_1)}{\cos \frac{\pi}{2\epsilon} (\xi - a_1) + \cosh \frac{\pi}{2\epsilon} (\lambda + \eta - \beta)} e^{-n\lambda} d\lambda \\
&= 2 \sum_{m=1}^{\infty} (-1)^{m+1} \int_0^{\infty} e^{-n\lambda} d\lambda \cdot e^{-\frac{m\pi}{2\epsilon} (\lambda + \eta - \beta)} \sin \frac{m\pi}{2\epsilon} (\xi - a_1) \\
&= 2 \sum_{m=1}^{\infty} (-1)^{m+1} \cdot \frac{e^{-\frac{m\pi}{2\epsilon} (\eta - \beta)}}{n + \frac{m\pi}{2\epsilon}} \sin \frac{m\pi}{2\epsilon} (\xi - a_1) \\
& \int_0^{\infty} \frac{\sin \theta_1 e^{-n\lambda} d\lambda}{\cos \theta_1 + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)} = \int_{\eta - \beta}^{\infty} \frac{\sin \theta_1 e^{-n\lambda} d\lambda}{\cos \theta_1 + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)} \\
& \quad + \int_0^{\eta - \beta} \frac{\sin \theta_1 e^{-n\lambda} d\lambda}{\cos \theta_1 + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)}
\end{aligned}$$

In the first integral on the right hand side  $\lambda - \eta + \beta$  is positive and in the second  $\lambda - \eta + \beta$  is negative.

Put  $x = \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)$

when  $x$  is positive

$$\frac{\sin \theta_1}{\cos \theta_1 + \cosh x} = 2 \sum_{m=1}^{\infty} (-1)^{m+1} e^{-mx} \sin m\theta_1$$

when  $x$  is negative

$$\frac{\sin \theta_1}{\cos \theta_1 + \cosh x} = 2 \sum_{m=1}^{\infty} (-1)^{m+1} e^{mx} \sin m\theta_1 ;$$

$$\begin{aligned}
& \int_{\eta-\beta}^{\infty} \frac{\sin \theta_1 e^{-n\lambda} d\lambda}{\cos \theta_1 + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)} \\
&= 2 \sum_{m=1}^{\infty} (-1)^{m+1} e^{\frac{m\pi}{2\epsilon} (\eta-\beta)} \sin m\theta_1 \int_{\eta-\beta}^{\infty} e^{-(n + \frac{m\pi}{2\epsilon})\lambda} d\lambda \\
&= 2 \sum_{m=1}^{\infty} (-1)^{m+1} e^{\frac{m\pi}{2\epsilon} (\eta-\beta)} \frac{e^{-n(\eta-\beta)}}{n + \frac{m\pi}{2\epsilon}} \sin m\theta_1 ; \\
& \int_0^{\eta-\beta} \frac{\sin \theta_1 e^{-n\lambda} d\lambda}{\cos \theta_1 + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)} \\
&= 2 \sum_{m=1}^{\infty} (-1)^{m+1} e^{-\frac{m\pi}{2\epsilon} (\eta-\beta)} \sin m\theta_1 \int_0^{\eta-\beta} e^{(-n + \frac{m\pi}{2\epsilon})\lambda} d\lambda \\
&= 2 \sum_{m=1}^{\infty} (-1)^{m+1} e^{-\frac{m\pi}{2\epsilon} (\eta-\beta)} \frac{e^{-n(\eta-\beta)} - e^{-\frac{m\pi}{2\epsilon} (\eta-\beta)}}{-n + \frac{m\pi}{2\epsilon}} \sin m\theta_1 . \\
&\therefore \int_0^{\infty} \frac{\sin \theta_1 e^{-n\lambda} d\lambda}{\cos \theta_1 + \cosh \frac{m\pi}{2\epsilon} (\lambda - \eta + \beta)} \\
&= 2e^{-n(\eta-\beta)} \sum_{m=1}^{\infty} (-1)^{m+1} \frac{4m\pi\epsilon}{m^2\pi^2 - 4n^2\epsilon^2} \sin m\theta_1 \\
&\quad - \frac{m\pi}{2\epsilon} (\eta-\beta) \\
&\quad - 4\epsilon \sum_{m=1}^{\infty} (-1)^{m+1} e^{\frac{m\pi}{2\epsilon} (\eta-\beta)} \frac{e^{-n(\eta-\beta)}}{m\pi - 2n\epsilon} \sin m\theta_1 .
\end{aligned}$$

But we have, when  $\xi$  lies between  $\alpha_1$  and  $\alpha_2$

$$\frac{\sin n(\xi - \alpha_1)}{\sin 2n\epsilon} = 2 \sum_{m=1}^{\infty} (-1)^{m+1} \frac{m\pi}{m^2\pi^2 - 4n^2\epsilon^2} \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_1) ;$$

$$\therefore \int_0^{\infty} \frac{\sin \frac{\pi}{2\epsilon} (\xi - a_1) e^{-n\lambda} d\lambda}{\cos \frac{\pi}{2\epsilon} (\xi - a_1) + \cosh \frac{\pi}{2\epsilon} (\lambda - \eta + \beta)}$$

$$= \frac{4e^{-n(\eta-\beta)} \sin n(\xi - a_1)}{\sin 2n\epsilon}$$

$$- 4\epsilon \sum_{m=1}^{\infty} (-1)^{m+1} \frac{e^{-\frac{m\pi}{2\epsilon} (\eta-\beta)}}{m\pi - 2n\epsilon} \sin \frac{m\pi}{2\epsilon} (\xi - a_1)$$

$$\therefore I_1 = \frac{\pi}{2} \left[ \frac{\sin n(\xi - a_1)}{\sin 2n\epsilon} e^{-n(\eta-\beta)} \right.$$

$$\left. - \sum_{m=1}^{\infty} (-1)^{m+1} \frac{2m\pi}{m^2\pi^2 - 4n^2\epsilon^2} \sin \frac{m\pi}{2\epsilon} (\xi - a_1) e^{-\frac{m\pi}{2\epsilon} (\eta-\beta)} \right].$$

$$\therefore \sum_{n=1}^{\infty} \left\{ R_n \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \frac{\sinh a(\xi - a_1)}{\sinh 2a\epsilon} \sin a\lambda \sin a(\eta - \beta) da \right.$$

$$\left. + S_n \int_0^{\infty} e^{-n\lambda} d\lambda \int_0^{\infty} \frac{\sinh a(\xi - a_2)}{\sinh 2a\epsilon} \sin a\lambda \sin a(\eta - \beta) da \right\}$$

$$= 2 \sum_{n=1}^{\infty} (-1)^{n+1} e^{-n\beta}$$

$$\times \coth \beta \frac{\cos na_2 \sin n(\xi - a_1) - \cos na_1 \sin n(\xi - a_2)}{\sin 2n\epsilon} e^{-n(\eta-\beta)}$$

$$+ 2 \sum_{n=1}^{\infty} (-1)^{n+1} e^{-n\beta} \coth \beta \sum_{m=1}^{\infty} (-1)^m \frac{2m\pi}{m^2\pi^2 - 4n^2\epsilon^2}$$

$$\times e^{-\frac{m\pi}{2\epsilon} (\eta-\beta)} \left[ \cos na_2 \sin \frac{m\pi}{2\epsilon} (\xi - a_1) - \cos na_1 \sin \frac{m\pi}{2\epsilon} (\xi - a_2) \right]$$

$$= 2 \coth \beta \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\cos n\alpha_2 \sin n(\xi - \alpha_1) - \cos n\alpha_1 \sin n(\xi - \alpha_2)}{\sin 2n\epsilon} e^{-n\eta}$$

$$+ 4 \sum_{m=1}^{\infty} \left\{ A_m \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_1) + B_m \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_2) \right\} e^{-\frac{m\pi}{2\epsilon} (\eta - \beta)} \quad (6)$$

where

$$A_m = \sum_{n=1}^{\infty} (-1)^{m+n+1} \frac{m\pi}{m^2\pi^2 - 4n^2\epsilon^2} e^{-\eta\beta} \coth \beta \cos n\alpha_2 \quad \dots \quad (7)$$

$$B_m = \sum_{n=1}^{\infty} (-1)^{m+n} \frac{m\pi}{m^2\pi^2 - 4n^2\epsilon^2} e^{-\eta\beta} \coth \beta \cos n\alpha_1.$$

But  $\cos n\alpha_2 \sin n(\xi - \alpha_1) - \cos n\alpha_1 \sin n(\xi - \alpha_2)$

$$= \cos n\xi \sin n(\alpha_2 - \alpha_1);$$

therefore

$$\psi = 2c^2\omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin n\alpha_2 \cot \alpha_2 \sin n(\xi - \alpha_1) + \sin n\alpha_1 \cot \alpha_1 \sin n(\alpha_2 - \xi)}{\sin n(\alpha_2 - \alpha_1)} e^{-n\eta}$$

$$+ 4c^2\omega \sum_{m=1}^{\infty} \left\{ A_m \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_1) + B_m \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_2) \right\} e^{-\frac{m\pi}{2\epsilon} (\eta - \beta)}$$

$$+ 4c^2\omega \sum_{m=0}^{\infty} C_m \cos \frac{(2m+1)\pi}{2\epsilon} (\xi - \gamma) e^{-\frac{(2m+1)\pi}{2\epsilon} (\eta - \beta)} \quad \dots \quad (8)$$

where

$$C_m = \sum_{n=1}^{\infty} (-1)^{m+n+1} \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon^2}$$

$$\times (\sin n\alpha_2 \cot \alpha_2 + \sin n\alpha_1 \cot \alpha_1) e^{-\eta\beta}; \quad \dots \quad (9)$$

therefore

$$\begin{aligned} \phi = & 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin na_2 \cot a_2 \cos n(\xi - a_1) - \sin na_1 \cot a_1 \cos n(\xi - a_2)}{\sin n(a_2 - a_1)} e^{-n\eta} \\ & + 4c^2 \omega \sum_{m=1}^{\infty} \{A_m \cos \frac{m\pi}{2\epsilon} (\xi - a_1) + B_m \cos \frac{m\pi}{2\epsilon} (\xi - a_2)\} e^{-\frac{m\pi}{2\epsilon} (\eta - \beta)} \\ & - 4c^2 \omega \sum_{m=0}^{\infty} C_m \sin \frac{(2m+1)\pi}{2\epsilon} (\xi - \gamma) e^{-\frac{(2m+1)\pi}{2\epsilon} (\eta - \beta)} \dots \quad (10) \end{aligned}$$

4 The following particular cases can be deduced from the case of three circles.

(1) *Two orthogonal circles*

Put  $a_2 = a$  and  $a_1 = -(\pi - a)$

$\therefore$  we get an area bounded by two orthogonal circles.

$$2\epsilon = \pi \text{ and } 2\gamma = 2a - \pi$$

then after a little simplification we have

$$\begin{aligned} \psi = & 2c^2 \omega \cot a \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \sin n\xi \\ & + 4c^2 \omega \cot a \sum_{m=1}^{\infty} M \sin m(\xi - a) e^{-m(\eta - \beta)} \\ & + 4c^2 \omega \sum_{m=1}^{\infty} N \sin (2m+1)(\xi - a) e^{-(2m+1)(\eta - \beta)} \end{aligned}$$

where

$$M = \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{m}{m^2 - n^2} e^{-n\beta} \coth \beta \cos na \left[ (-1)^{n+1} + (-1)^n \right]$$

and

$$N = \frac{2}{\pi} \sum_{p=1}^{\infty} \frac{(2m+1)}{(2m+1)^2 - 4p^2} \cot \alpha \sin 2pa \cdot e^{-\frac{1}{2} p \beta}$$

The expression for  $\phi$  can be written down.

(2) *Semi-lune*

If we put  $\beta=0$ , we get an area bounded by two circles and a straight line cutting them at right angles.

The boundary condition for  $\beta=0$  is

$$\begin{aligned} \psi &= \lim_{\eta=0} c\omega y \coth \eta \\ &= \lim_{\eta=0} \frac{c + 2c \sum_{n=1}^{\infty} (-1)^n e^{-n\eta} \cos n\xi}{1} \\ &= \lim_{\eta=0} c\omega \frac{2c \sum_{n=1}^{\infty} (-1)^{n+1} n e^{-n\eta} \cos n\xi}{\operatorname{sech}^2 \eta} \\ &= 2c^2 \omega \sum_{n=1}^{\infty} (-1)^{n+1} n \cos n\xi. \end{aligned}$$

The boundary condition when  $\eta=\beta$  is

$$\psi = 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n e^{-n\beta} \coth \beta \cos n\xi$$

Replacing  $e^{-n\beta} \coth \beta$  by  $-n$  we have

$$\begin{aligned} \psi &= 2c^2 \omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin n\alpha_2 \cot \alpha_2 \sin n(\xi - \alpha_1) + \sin n\alpha_1 \cot \alpha_1 \sin n(\alpha_2 - \xi)}{\sin n(\alpha_2 - \alpha_1)} e^{-n} \\ &\quad + 4c^2 \omega \sum_{m=1}^{\infty} \left\{ A_m \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_1) + B_m \sin \frac{m\pi}{2\epsilon} (\xi - \alpha_2) \right\} e^{-\frac{m\pi}{2\epsilon} \eta} \\ &\quad + 4c^2 \omega \sum_{m=0}^{\infty} C_m \cos \frac{(2m+1)\pi}{2\epsilon} (\xi - \gamma) e^{-\frac{(2m+1)\pi}{2\epsilon} \eta} \end{aligned}$$



where

$$A_m = \sum_{n=1}^{\infty} (-1)^{m+n} \frac{mn\pi}{m^2\pi^2 - 4n^2\epsilon^2} \cos n\alpha_2$$

$$B_m = \sum_{n=1}^{\infty} (-1)^{m+n+1} \frac{mn\pi}{m^2\pi^2 - 4n^2\epsilon^2} \cos n\alpha_1$$

$$C_m = \sum_{n=1}^{\infty} (-1)^{m+n+1} \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - 4n^2\epsilon^2} (\sin n\alpha_2 \cot \alpha_2 + \sin n\alpha_1 \cot \alpha_1)$$

(3) Area bounded by a circle and two chords at right angles.

Put  $\beta=0$ ,  $\alpha_1=0$ ,  $\alpha_2=a$

$$\therefore 2\gamma=a, 2\epsilon=a$$

$$\psi = 2c^2\omega \sum_{n=1}^{\infty} (-1)^n \frac{\sin n\alpha [\cot \alpha \sin n\xi + n \sin n(a-\xi)]}{\sin n\alpha} e^{-n\eta}$$

$$+ 4c^2\omega \sum_{m=1}^{\infty} L_m \sin \frac{m\pi\xi}{a} e^{-\frac{m\pi\eta}{a}}$$

$$+ 4c^2\omega \sum_{m=0}^{\infty} D_m \sin \frac{(2m+1)\pi\xi}{a} e^{-\frac{(2m+1)\pi\eta}{a}}$$

where

$$L_m = \sum_{n=1}^{\infty} (-1)^n \frac{mn\pi}{m^2\pi^2 - n^2a^2} [(-1)^m \cos na - 1]$$

$$D_m = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(2m+1)\pi}{(2m+1)^2\pi^2 - n^2a^2} (\sin na \cot a + n).$$

# ON THE FUNDAMENTAL THEOREM OF THE INTEGRAL CALCULUS

BY  
GANESH PRASAD

According to the fundamental theorem of the Integral Calculus, the integral function

$$F(x) \equiv \int f(x) dx$$

has a differential coefficient  $f(x)$  at any point of continuity of  $f(x)$ . But the usual proof to be found in books on the theory of functions of a real variable fails altogether when we consider the question of the existence of the differential coefficient of  $F(x)$  at a point where  $f(x)$  has a discontinuity of the *second* kind.

The object of the present paper is to investigate the conditions, which must be satisfied by  $f(x)$  or the types of functions to which  $f(x)$  must belong, in order that  $F(x)$  should have a differential coefficient at a point of discontinuity of the second kind of  $f(x)$ . The results obtained by me are believed to be all new.

For the sake of simplicity and fixity of ideas, I take the point of discontinuity to be  $x=0$  and represent the integral function as

$$\int_0^x f(x) dx.$$

Throughout the paper  $\psi(x)$  denotes a function which is monotone in the neighbourhood of  $x=0$  and which tends to infinity as  $x$  tends to 0.

$$\text{I. } \underline{f'(x)} = \cos \psi(x)$$

§ 1. Let  $f(x) = \cos \psi(x)$ .

Then, at  $x=0$ ,  $F(x)$  has a differential coefficient equal to zero when

$$\psi(x) \sim \log \left( \frac{1}{x^2} \right),$$

and  $F(x)$  has no differential coefficient when

$$\psi(x) \leq \log \left( \frac{1}{x^2} \right).$$

*Proof:—*

$$(a) \text{ Case: } \psi(x) \geq \log \left( \frac{1}{x^2} \right).$$

Since

$$\frac{d}{dx} \left\{ \frac{1}{\psi'} \sin \psi \right\} = \cos \psi - \frac{\psi''}{(\psi')^2} \sin \psi,$$

integrating both the sides of the above equality, we have

$$\frac{1}{\psi'} \sin \psi = \int_0^x \cos \psi \, dx - \int_0^x \frac{\psi''}{(\psi')^2} \sin \psi \, dx,$$

i.e.,

$$\int_0^x \cos \psi \, dx = \frac{\sin \psi}{\psi'} + \int_0^x \frac{\psi''}{(\psi')^2} \sin \psi \, dx.$$

Now consider

$$\lim_{x \rightarrow +0} \frac{F(x)}{x}.$$

This equals

$$\lim_{x \rightarrow +0} \frac{\sin \psi}{x\psi'} + \lim_{x \rightarrow +0} \frac{1}{x} \int_0^x \frac{\psi''}{(\psi')^2} \sin \psi \, dx. \quad \dots (1)$$

But, since

$$\psi \geq \log \frac{1}{x^2}$$

$$\psi' \geq \frac{1}{x},$$

i.e.,

$$\psi' \geq 1;$$

also

$$\frac{\psi''}{(\psi')^2} < 1$$

and consequently

$$\frac{\psi''}{(\psi')^2} \sin \psi$$

is continuous at  $x=0$ . Therefore both the limits in (1) exist and equal zero. Therefore

$$\lim_{x \rightarrow +0} \frac{F(x)}{x}$$

exists and equals zero.

Similarly it can be proved that

$$\lim_{x \rightarrow -0} \frac{F(x)}{x}$$

exists and equals zero.

Hence  $F'(0)$  exists and equals zero.

(b) Case:  $\psi(x) \sim \log \left( \frac{1}{x^2} \right).$

Integrating by parts,

$$\int_0^x \cos \psi \, dx = x \cos \psi + \int_0^x x \psi' \sin \psi \, dx.$$

Now,

$$\psi' \sim \frac{1}{x}, \text{ i.e., } x\psi' \sim 1.$$

Therefore  $x\psi' \sin \psi$  is continuous at  $x=0$  and, consequently,

$$\int_0^x x \psi' \sin \psi \, dx$$

has a differential coefficient zero at  $x=0$ . Therefore, at  $x=0$ ,  $F(x)$  has no differential coefficient, for  $x \cos \psi$  has no differential coefficient there.

(c) Case:  $\psi(x) \sim \log \left( \frac{1}{x^2} \right).$

Let

$$\psi(x) = a + \log \frac{1}{x^2},$$

where  $\alpha$  is a constant, and  $x$  is positive. Then,

$$\begin{aligned}
 F(x) &= \cos \alpha \int_0^x \cos \log \frac{1}{x} dx - \sin \alpha \int_0^x \sin \log \frac{1}{x} dx \\
 &= x \cos \alpha \cdot \frac{\cos \log \frac{1}{x} - \sin \log \frac{1}{x}}{2} - x \sin \alpha \cdot \frac{\cos \log \frac{1}{x} + \sin \log \frac{1}{x}}{2} \\
 &= x \cos \log \frac{1}{x} \cdot \frac{\cos \alpha - \sin \alpha}{2} - x \sin \log \frac{1}{x} \cdot \frac{\cos \alpha + \sin \alpha}{2} \\
 &= \frac{x}{\sqrt{2}} \cos \left\{ \alpha + \log \frac{1}{x} + \frac{\pi}{4} \right\} \\
 &= \frac{x}{\sqrt{2}} \cos \left( \psi + \frac{\pi}{4} \right).
 \end{aligned}$$

Therefore, whatever  $\alpha$  may be,  $F'(0)$  is non-existent.

Generally, let

$$\psi(x) = \frac{1}{2} \left\{ \sigma(x) + 1 \right\} \log \frac{1}{x},$$

where  $\sigma(x) \rightarrow 1$ .

Then, proceeding as in (b), we have

$$\begin{aligned}
 \int_0^x \cos \psi dx &= x \cos \psi + \int_0^x x \psi' \sin \psi dx \\
 &= x \cos \psi + \int_0^x \left\{ x \sigma' \log \frac{1}{x} - (1 + \sigma) \right\} \sin \psi dx \\
 &= x \cos \psi - \int_0^x \sin \psi dx + G(x),
 \end{aligned}$$

where  $G$ , being the integral function of a continuous integrand which tends to 0 with  $x$ , has a differential coefficient zero at  $x=0$ .

Therefore in the limit we may take

$$\int_0^x \cos \psi \, dx = x \cos \psi - \int_0^x \sin \psi \, dx.$$

Similarly

$$\int_0^x \sin \psi \, dx = x \sin \psi + \int_0^x \cos \psi \, dx.$$

Therefore, as  $x$  tends to zero,

$$\int_0^x \cos \psi \, dx$$

behaves as

$$x \cdot \frac{\cos \psi - \sin \psi}{2},$$

i.e., as

$$\frac{x}{\sqrt{2}} \cos \left( \psi + \frac{\pi}{4} \right).$$

Hence  $F'(0)$  is non-existent.

## II. $f(x) = \chi(x) \cos \psi(x)$ , $\chi$ being monotone and limited

§ 2. If  $f(x) = \chi(x) \cos \psi(x)$ , where  $\chi(x)$  is monotone and of the form  $A + \chi_1(x)$ ,  $A$  being a constant, different from zero, and  $\chi_1 \prec 1$ , then  $F'(0)$  exists or not according as

$$\psi \succ \log \frac{1}{x^2} \quad \text{or} \quad \psi \preceq \log \frac{1}{x^2}.$$

*Example.*

$$\int_0^x \left( 1 + \sqrt{x} \right) \cos \frac{1}{x} \, dx$$

has a differential coefficient zero at  $x=0$ .

### III. $f(x) = \chi(x) \cos \psi(x)$ , $\chi$ being limited but not monotone

§ 3. Let  $f(x) = \chi(x) \cos \psi(x)$ , where  $\chi(x)$  is not monotone but is of the form  $A + \chi_1(x)$ ,  $A$  being a constant different from zero and  $\chi_1$  being equal to  $B \cos \psi_1(x)$ , where  $B$  is a constant different from zero and  $\psi_1 \succ 1$ .

Then  $F'(0)$  exists or not according as

$$\psi \succ \log \frac{1}{x^2}, \quad \text{or} \quad \psi \preceq \log \frac{1}{x^2},$$

$\psi_1$  not being  $\sim \psi$ .

*Proof:*—

$$\begin{aligned} F(x) &= \int_0^x (A + B \cos \psi_1) \cos \psi \, dx \\ &= A \int_0^x \cos \psi \, dx + \frac{B}{2} \int_0^x \cos (\psi + \psi_1) \, dx + \frac{B}{2} \int_0^x \cos (\psi - \psi_1) \, dx \dots \quad (2) \end{aligned}$$

Now, when  $\psi \succ \log \frac{1}{x^2}$ ,

$$\psi + \psi_1 \succ \log \frac{1}{x^2}, \quad \text{and also} \quad \psi - \psi_1 \succ \log \frac{1}{x^2}.$$

Therefore by § 1, each of the three integral functions in the equation (2) to whose sum  $F(x)$  is equal has a differential coefficient zero at  $x=0$ ; consequently  $F'(0)$  exists and is zero.

When  $\psi \preceq \log \frac{1}{x^2}$ ,

then two cases arise; either

$$\psi_1 \succ \log \frac{1}{x^2}, \quad \text{or} \quad \psi_1 \preceq \log \frac{1}{x^2}.$$

In the first case the second and the third integral functions in (2) have each zero as their differential coefficients at  $x=0$ , and the first

integral function has no differential coefficient. Hence  $F'(0)$  is non-existent. In the second case there are three possibilities according as

$$(i) \quad \psi \asymp \log \frac{1}{x^2} \text{ and } \psi_1 \asymp \log \frac{1}{x^2},$$

$$(ii) \quad \psi \asymp \log \frac{1}{x^2} \text{ and } \psi_1 \asymp \log \frac{1}{x^2},$$

or

$$(iii) \quad \psi \asymp \log \frac{1}{x^2} \text{ and } \psi_1 \asymp \log \frac{1}{x^2}.$$

For (i), it follows from (b) of § 1, that  $\frac{F(x)}{x}$  behaves as

$$A \cos \psi + \frac{B}{2} \cos (\psi + \psi_1) + \frac{B}{2} \cos (\psi - \psi_1),$$

and therefore  $F'(0)$  is non-existent.

For (ii), it follows from (b) and (c) of § 1 that  $\frac{F(x)}{x}$  behaves as

$$A \cos \psi + \frac{B}{2\sqrt{2}} \cos \left( \psi + \psi_1 + \frac{\pi}{4} \right) + \frac{B}{2\sqrt{2}} \cos \left( \psi - \psi_1 + \frac{\pi}{4} \right),$$

and therefore  $F'(0)$  is non-existent.

For (iii), it follows from (c) of § 1 that  $\frac{F(x)}{x}$  behaves as

$$\begin{aligned} \frac{A}{\sqrt{2}} \cos \left( \psi + \frac{\pi}{4} \right) + \frac{B}{2\sqrt{2}} \cos \left( \psi + \psi_1 + \frac{\pi}{4} \right) \\ + \frac{B}{2\sqrt{2}} \cos \left( \psi - \psi_1 + \frac{\pi}{4} \right) \end{aligned}$$

and therefore  $F'(0)$  is non-existent.

*Examples.*

$$(1) \quad \int_0^x \cos^2 \left( \log \frac{1}{x^2} \right) \cos \frac{1}{x} dx$$

has a differential coefficient zero at  $x=0$ .



$$(2) \quad \int_0^x \cos^2 \left( \log \frac{1}{x^2} \right) \sin \left\{ \left( \log \frac{1}{x^2} \right)^{\frac{1}{2}} \right\} dx$$

has no differential coefficient at  $x=0$ .

§ 4. Consider now the case of  $\psi_1 \smile \psi$  and let  $\psi_1 = \psi(A + \sigma)$  where  $A$  is a constant different from zero and  $\sigma < 1$ . A number of cases arise.

(i) If  $\psi > \log \frac{1}{x^2}$ , the first two integral functions of equation (2) of the previous article have each zero as their differential coefficients at  $x=0$ ; consequently  $F'(0)$  exists or not according as

$$(\psi - \psi_1) > \log \frac{1}{x^2}, \text{ or } (\psi - \psi_1) \leq \log \frac{1}{x^2},$$

which latter case can be possible only if  $A=1$ ; provided that it is understood that  $F'(0)$  always exists if  $(\psi - \psi_1) \smile 1$ .

(ii) If  $\psi < \log \frac{1}{x^2}$ , then  $(\psi + \psi_1) \prec \log \frac{1}{x^2}$  and either

$$1 \prec (\psi - \psi_1) \prec \log \frac{1}{x^2}, \text{ or } (\psi - \psi_1) \smile 1.$$

Therefore in this case it is easily proved by proceeding as in the preceding article that  $F'(0)$  is non-existent.

(iii) If  $\psi \smile \log \frac{1}{x^2}$ , then  $(\psi + \psi_1) \smile \log \frac{1}{x^2}$  and either

$$1 \prec (\psi - \psi_1) \leq \log \frac{1}{x^2}, \text{ or } (\psi - \psi_1) \smile 1.$$

Therefore in this case it is easily proved by proceeding as in the preceding article that  $F'(0)$  is non-existent.

*Examples.*

$$(1) \quad \int_0^x \left( 1 + \cos \frac{1}{x} \right) \cos \frac{1}{x} dx$$

has a differential coefficient at  $x=0$  and is equal to  $\frac{1}{2}$ .

$$(2) \quad \int_0^x \left( 1 + \cos \log \frac{1}{x^2} \right) \cos \log \frac{1}{x^2} dx$$

has no differential coefficient at  $x=0$ .

$$(3) \quad \int_0^x \left\{ 1 + \cos \sqrt{\log \frac{1}{x^2}} \right\} \cos \log \frac{1}{x^2} dx$$

has no differential coefficient at  $x=0$ .

$$(4) \quad \int_0^x \cos^2 \log \frac{1}{x^2} \cdot \sin \log \frac{1}{x^2} dx$$

has no differential coefficient at  $x=0$ .

#### IV. $f(x) = \chi(x) \cos \psi(x)$ , $\chi(x) > 1$

§ 5. Let  $f(x) = \chi(x) \cos \psi(x)$ ,

where  $\chi(x)$  is monotone in the neighbourhood of  $x=0$  and tends to infinity as  $x$  tends to zero. Then assuming that the improper integral

$$t \equiv \int_0^x \chi(x) dx$$

exists and  $F(x)$  becomes

$$\int_0^t \cos \{ \phi(t) \} dt,$$

$\phi(t)$  standing for  $\psi(x)$ , the criteria of § 1 are applicable.

*Examples.*

$$(1) \quad \int_0^x \frac{1}{\sqrt{x}} \cos \frac{1}{\sqrt{x}} dx$$

has a differential coefficient at  $x=0$ .

$$(2) \quad \int_0^x \frac{1}{x^p} \cos \frac{1}{x^k} dx$$

has a differential coefficient at  $x=0$ ,  $p$  being any positive proper fraction and  $k$  being any constant greater than zero.

$$(3) \quad \int_0^x \frac{1}{\sqrt{x}} \cos \left( \log \frac{1}{x^2} \right) dx$$

has no differential coefficient at  $x=0$ .

$$(4) \quad \int_0^x \frac{1}{x \left( \log \frac{1}{x^2} \right)^2} \cos \left( \log \frac{1}{x^2} \right) dx$$

has a differential coefficient zero at  $x=0$ .

**V.  $f(x) = \chi(x) \cos \psi(x)$ ,  $\chi(x)$  being neither limited nor monotone**

§ 6. If  $f(x) = \chi(x) \cos \psi(x)$ , where  $\chi(x)$  is not monotone but makes an infinite number of fluctuations with indefinitely increasing amplitudes as  $x$  tends to zero, the procedures of the preceding articles cease to be applicable and in each case a special procedure is necessary.

*Examples,*

$$(1) \quad \text{Let} \quad f(x) = \left\{ 1 + \frac{1}{x} e^{\frac{1}{x}} \tan \left( e^{\frac{1}{x}} \right) \right\} \cos \left( e^{\frac{1}{x}} \right).$$

Then

$$\int_0^x f(x) dx = x \cos \left( e^{\frac{1}{x}} \right).$$

Therefore  $F'(0)$  is non-existent.

$$(2) \quad \text{Let} \quad f(x) = \left\{ 1 + \frac{1}{x} \tan \left( \frac{1}{x} \right) \right\} \cos \left( \frac{1}{x} \right).$$

$$\text{Then} \quad \int_0^x f(x) dx = x \cos \frac{1}{x}.$$

Therefore  $F'(0)$  is non-existent.

$$(3) \quad \text{Let} \quad f(x) = \left\{ (1+k-p)x^{k-p} + \frac{k}{x^p} \tan \left( \frac{1}{x^k} \right) \right\} \cos \left( \frac{1}{x^k} \right),$$

where  $k$  and  $p$  are both greater than zero. Then

$$\int_0^x f(x) dx = x^{1+k-p} \cos \frac{1}{x^k}.$$

Therefore  $F'(0)$  is existent or non-existent according as  $k > p$  or not.

§ 7. If  $f(x)$  makes an infinite number of fluctuations, not only in the neighbourhood of  $x=0$  but also in the neighbourhood of any point  $x=\omega_n$ ,  $\{\omega_n\}$  being an enumerable and everywhere dense aggregate with 0 as a limiting point, then the procedures of the preceding articles cease to be applicable.

*Example.*

$$(1) \quad \text{Let} \quad f(x) = \sum_{n=1}^{\infty} \frac{1}{2^n} \cos \frac{1}{x-\omega_n}, \quad \text{where } \{\omega_n\} \text{ is the aggregate of}$$

rational numbers with 0 as a limiting point.

Now

$$\begin{aligned} & \frac{d}{dx} \left[ \sum_{n=1}^{\infty} (x-\omega_n)^2 \frac{1}{2^n} \sin \frac{1}{x-\omega_n} \right] \\ &= - \sum_{n=1}^{\infty} \frac{1}{2^n} \cos \frac{1}{x-\omega_n} + 2 \sum_{n=1}^{\infty} \frac{1}{2^n} (x-\omega_n) \sin \frac{1}{x-\omega_n}, \end{aligned}$$

term-by-term differentiation being permissible, as all the series concerned are uniformly convergent. Hence, integrating, we have

$$\begin{aligned} & \left[ -\sum_1^{\infty} (x-\omega_n) \cdot \frac{1}{2^n} \sin \frac{1}{x-\omega_n} \right]_0^x \\ & + 2 \int_0^x \left\{ \sum_1^{\infty} \frac{1}{2^n} (x-\omega_n) \sin \frac{1}{x-\omega_n} \right\} dx \\ & = \int_0^x f(x) dx. \end{aligned}$$

But obviously each of the two terms on the left side in the above equation has a differential coefficient for  $x=0$ . Therefore  $F'(0)$  exists.

## TIDAL OSCILLATIONS ON A SPHEROID

By

B. M. SEN

The problem of tides on a globe was initiated by Laplace\* and was further developed by Kelvin, Darwin, Airy and Hough. In his treatment of the tides on rotating globe, Laplace found the dynamical equations of tidal oscillations on a spheroid but passed off at once to the globe neglecting the eccentricity of the meridian section. The assumptions on which his treatment was based were the following :

(1) The motion is supposed small, so that the product and squares of the velocity are neglected.

(2) The pressure is the same as the hydrostatic pressure.

These are the usual assumptions of tidal oscillations.

(3) The free surface is an equipotential surface and the depth  $h$  of the liquid is supposed small, but arbitrary.

This implies that the surface of the spheroid is an equipotential surface or only slightly different from an equipotential surface.

(4) The ratio of the centrifugal force at the equator to the gravity,  $\omega^2 a/g$ , is supposed small.

(5) The eccentricity is neglected in the subsequent treatment.

(6) The attraction of the layer of liquid is neglected ; this has been taken into account by subsequent writers.

In the following pages the problem of tidal oscillations on a spheroid rotating as well as non-rotating is dealt with. The eccentricity of the meridian section is not assumed small ; the problem, moreover, differs from that of motion on a globe by the fact that  $h$  is prescribed by the necessary condition that the surface of the spheroid and also the free surface must be equipotential surfaces.

\* Full references are given in Lamb's *Hydrodynamics*, Art. 213 *et seq.*

§ 1. Let the equation of the planetary spheroid be

$$\frac{x^2}{a^2} + \frac{y^2+z^2}{b^2} = 1, \quad \dots (1)$$

Introducing the spheroidal co-ordinates,

$$x = c\xi\zeta, \quad \omega = c\sqrt{1-\xi^2} \times \sqrt{1+\xi^2}, \quad \dots (2)$$

the spheroid is given by the equation

$$\zeta = a, \text{ a constant.}$$

Then

$$\delta s^2 = \frac{1}{h_1^2} \delta \xi^2 + \frac{1}{h_2^2} \delta \zeta^2 + \frac{1}{h_3^2} \delta \phi^2, \quad \dots (3)$$

$\delta s$  being an element of length in space where

$$h_1 = \frac{1}{c} \left( \frac{1-\xi^2}{\xi^2+\zeta^2} \right)^{\frac{1}{2}}, \quad h_2 = \frac{1}{c} \left( \frac{1+\xi^2}{\xi^2+\zeta^2} \right)^{\frac{1}{2}},$$

$$h_3 = \frac{1}{c} \frac{1}{(1-\xi^2)^{\frac{1}{2}} (1+\xi^2)^{\frac{1}{2}}}. \quad \dots (4)$$

§ 2. Consider first the case of no rotation. Let the depth of the liquid be  $h$  which is taken to be small. Neglecting the mutual attraction of the liquid particles, for equilibrium it is necessary that the surface of the spheroid be an equipotential. Now the potential of a solid homogeneous ellipsoid is given by the equation \*

$$V = -\pi \rho abc \{ \chi' - ax^2 - \beta y^2 - \gamma z^2 \}, \quad \dots (5)$$

where

$$\chi' = \int_{\lambda}^{\infty} \frac{du}{Q}, \quad \alpha = \int_{\lambda}^{\infty} \frac{du}{(a^2+u)Q}, \text{ etc.}$$

and

$$Q^2 = (a^2+u)(b^2+u)(c^2+u).$$

In no case except that of the sphere, can the surface of the ellipsoid be an equipotential. We, therefore, make the assumption that the

\* Routh, *Analytical Statics*, Vol. II, Art. 223, the sign of  $V$  having been reversed.

spheroid is heterogeneous and its equipotential surfaces are confocal spheroids. These are given by the relation  $\zeta = \text{const.}$ , and  $V$  is a function of  $\zeta$  only.

§ 3. The equation of the meridian section is

$$\frac{x^2}{\zeta^2} + \frac{\omega^2}{1 + \zeta^2} = c^2. \quad \dots (6)$$

As the thin layer of liquid is encased between two confocal spheroids, the depth  $h$  is given by the relation.

$$h = \frac{d\zeta}{h_2} = \frac{\kappa}{h_2}; \quad \dots (7)$$

where  $\kappa$  is a constant. If  $\chi$  be the height of the liquid above the undisturbed surface, the pressure at a height  $H$  above the surface of the spheroid is given by

$$\frac{P}{\rho} = C + g(h + \chi - H), \quad \dots (8)$$

with the usual assumptions that the pressure is the same as the hydrostatic pressure and the variation of gravity along  $h$  is neglected.

Now 
$$g = + \left[ \frac{\partial V}{\partial n} \right]_{\zeta=a} = + \left[ h_2 \frac{\partial V}{\partial \zeta} \right]_{\zeta=a}. \quad \dots (9)$$

As  $V$  is a function of  $\zeta$  only,  $\frac{\partial V}{\partial n}$  is a constant on the surface of the spheroid. Putting

$$f = + \left[ \frac{\partial V}{\partial \zeta} \right]_{\zeta=a},$$

we have

$$g = + h_2 f, \text{ where } f \text{ is a constant.} \quad \dots (10)$$

We have, therefore,

$$\begin{aligned} \frac{P}{\rho} &= \text{Const.} + f h_2 \left( \frac{\kappa}{h_2} + \chi \right), \\ &= \text{Const.} + f h_2 \chi. \end{aligned} \quad \dots (11)$$



§ 4. Denoting by  $u$  and  $w$  the velocities in the direction of  $\xi$  and  $\phi$  respectively, the hydrodynamical equations are

$$\frac{\partial u}{\partial t} = -\frac{h_1}{\rho} \cdot \frac{\partial P}{\partial \xi} - h_1 \frac{\partial \Omega}{\partial \xi} = -f h_1 \frac{\partial}{\partial \xi} \left( h_1 \chi + \frac{\Omega}{f} \right), \quad \dots \quad (12)$$

$$\frac{\partial w}{\partial t} = -\frac{h_2}{\rho} \cdot \frac{\partial P}{\partial \phi} - h_2 \frac{\partial \Omega}{\partial \phi} = -f h_2 \frac{\partial}{\partial \phi} \left( h_2 \chi + \frac{\Omega}{f} \right), \quad \dots \quad (13)$$

where  $\Omega$  is the potential of the disturbing forces.

The equation of continuity is

$$\begin{aligned} & -\frac{\partial}{\partial \xi} \left( h \frac{\delta \phi}{h_s} u \right) \delta \xi - \frac{\partial}{\partial \phi} \left( h \frac{\delta \xi}{h_1} w \right) \delta \phi \\ & = \frac{d}{dt} \left( \frac{\delta \xi}{h_1} \frac{\delta \phi}{h_s} \chi \right), \end{aligned}$$

or 
$$\frac{1}{h_s h_1} \frac{d\chi}{dt} = -\kappa \frac{\partial}{\partial \xi} \left( \frac{u}{h_s h_s} \right) - \kappa \frac{\partial}{\partial \phi} \left( \frac{w}{h_1 h_s} \right). \quad \dots \quad (14)$$

Differentiating (14) with respect to  $t$  and substituting from (12) and (13), we have the equation satisfied by  $h_s \chi$ .

$$\begin{aligned} \frac{1}{h_1 h_s h_s} \frac{d^2}{dt^2} (h_s \chi) &= f \kappa \left[ \frac{\partial}{\partial \xi} \left\{ \frac{h_1}{h_s h_s} \frac{\partial}{\partial \xi} \left( h_s \chi + \frac{\Omega}{f} \right) \right\} \right. \\ & \left. + \frac{\partial}{\partial \phi} \left\{ \frac{h_2}{h_1 h_s} \frac{\partial}{\partial \phi} \left( h_s \chi + \frac{\Omega}{f} \right) \right\} \right]; \quad \dots \quad (15) \end{aligned}$$

or, 
$$\begin{aligned} c^2 (\xi^2 + \zeta^2) \frac{d^2 (h_s \chi)}{dt^2} &= f \kappa \left[ \frac{\partial}{\partial \xi} \left\{ (1 - \xi^2) \frac{\partial}{\partial \xi} \left( h_s \chi + \frac{\Omega}{f} \right) \right\} \right. \\ & \left. + \frac{\partial}{\partial \phi} \left\{ \frac{\xi^2 + \zeta^2}{(1 - \xi^2)(1 + \zeta^2)} \cdot \frac{\partial}{\partial \phi} \left( h_s \chi + \frac{\Omega}{f} \right) \right\} \right]. \quad \dots \quad (16) \end{aligned}$$

Assuming the motion is simple harmonic with time-factor  $e^{ist}$ , the equation (16) becomes

$$\begin{aligned} \frac{c^2 \sigma^2}{\kappa f} (\xi^2 + \alpha^2) h_2 \chi + \frac{\partial}{\partial \xi} \left\{ (1 - \xi^2) \frac{\partial}{\partial \xi} \left( h_2 \chi + \frac{\Omega}{f} \right) \right\} \\ + \frac{\xi^2 + \alpha^2}{(1 - \xi^2)(1 - \alpha^2)} \frac{\partial^2}{\partial \phi^2} \left( h_2 \chi + \frac{\Omega}{f} \right) = 0, \quad \dots (17) \end{aligned}$$

$\zeta$  being a constant equal to  $\alpha$ .

§ 5. Considering the case of free oscillations, we have putting  $\Omega = 0$ ,

$$\begin{aligned} \frac{c^2 \sigma^2}{\kappa f} (\xi^2 + \alpha^2) (h_2 \chi) + \frac{\partial}{\partial \xi} \left\{ (1 - \xi^2) \frac{\partial (h_2 \chi)}{\partial \xi} \right\} \\ + \frac{\xi^2 + \alpha^2}{(1 - \xi^2)(1 + \alpha^2)} \frac{\partial^2 (h_2 \chi)}{\partial \phi^2} = 0. \quad \dots (18) \end{aligned}$$

We may further take  $h_2 \chi \propto \frac{\cos}{\sin} n\phi$ , the equation reducing to the form

$$\begin{aligned} \frac{d}{d\xi} \left\{ (1 - \xi^2) \frac{d(h_2 \chi)}{d\xi} \right\} + (\xi^2 + \alpha^2) \left\{ \frac{c^2 \sigma^2}{\kappa f} \right. \\ \left. - \frac{n^2}{(1 - \xi^2)(1 + \alpha^2)} \right\} h_2 \chi = 0. \quad \dots (19) \end{aligned}$$

This is a linear differential equation with constant coefficients. The singularities are  $\xi = \pm 1$ . These points are however regular.

For a globe of radius  $a$ ,

$$a = \infty, c = 0, \text{ while } ca = a,$$

this equation reduces to equation (1) of Art 199 of Lamb's Hydrodynamics.

§ 6. Taking the particular case of oscillations symmetrical about the axis we have putting  $n = 0$ ,

$$\frac{d}{d\xi} \left\{ (1 - \xi^2) \frac{d(h_2 \chi)}{d\xi} \right\} + (\xi^2 + \alpha^2) \frac{c^2 \sigma^2}{\kappa f} (h_2 \chi) = 0. \quad \dots (20)$$

Putting  $A = \frac{c^2 \sigma^2}{\kappa f}$  and assuming as a solution

$$h_2 \chi = \xi^r (a_0 + a_1 \xi + a_2 \xi^2 + \dots),$$

we have as the Indicial equation

$$r(r-1) = 0. \quad \dots (21)$$

The successive coefficients are given by the relation

$$a_n = \frac{\{(n-1)(n-2) + Aa^2\}a_{n-2} + Aa_{n-4}}{n(n-1)}, \text{ when } n \geq 4 \dots (22)$$

$$a_n = \frac{\{(n-1)(n-2 + Aa^2)\}a_{n-2}}{n(n-1)}, \text{ when } n < 4. \quad \dots (23)$$

We may therefore write the solution in the form

$$h_2 \chi = \{a_0 + a_2 \xi^2 + a_4 \xi^4 + \dots\} + \{a_1 \xi + a_3 \xi^3 + a_5 \xi^5 + \dots\} \quad \dots (24)$$

§ 7. Consider the disturbing body moving in the plane of the equator at a distance  $R$  from the centre. If  $\gamma$  be the gravitational constant,  $M$  the mass,  $R$  the radius vector,  $\phi'$  the angle between the radius vector and the  $y$ -axis, the potential  $\Omega$  at a point on the surface is given by the equation

$$\begin{aligned} \Omega &= - \frac{\gamma M}{\{x^2 + (R \cos \phi' - y)^2 + (R \sin \phi' - z)^2\}^{1/2}} \\ &= - \frac{\gamma M}{R} \left\{ 1 + \frac{y \cos \phi' + z \sin \phi'}{R} - \frac{1}{2} \frac{x^2 + y^2 + z^2}{R^2} \right. \\ &\quad \left. + \frac{3}{2} \frac{(y \cos \phi' + z \sin \phi')^2}{R^2} \right\} \quad \dots (25) \end{aligned}$$

neglecting terms of higher order in  $\left(\frac{1}{R}\right)$ .

The second term represents the potential of a uniform force  $\frac{\gamma M}{R^2}$  in the direction of the disturbing body. The potential of the relative attraction is, therefore,

$$\frac{\gamma M}{R^3} \left\{ \frac{1}{2} (x^2 + y^2 + z^2) - \frac{3}{2} (y \cos \phi' + z \sin \phi')^2 \right\}.$$

Substituting this value in equation (17), we get the height of the tidal wave, though the equation becomes unmanageable.

§ 8. If the spheroid has an angular velocity  $\omega$  about the  $x$ -axis which is taken into account, the problem becomes more complicated. The surface of the spheroid is, as before, an equipotential surface under the gravitational force and the centrifugal force. In fact, if the spheroid is taken to be homogeneous the surface is that of a solidified MacLaurin's spheroid. Making this assumption and taking the equation (1) as the equation of the surface, the gravitational potential at the surface can be written in the form

$$\Omega = \pi\rho\{a_0x^2 + \beta_0y^2 + \beta_0z^2 - \chi_0\} \quad \dots (26)$$

where 
$$a_0 = abc \int_0^\infty \frac{du}{(a^2+u)\Delta}, \quad \beta_0 = abc \int_0^\infty \frac{du}{(b^2+u)\Delta},$$

$$\chi_0 = abc \int_0^\infty \frac{du}{\Delta}, \text{ and } \Delta^2 = (a^2+u)(b^2+u)^2. \quad \dots (27)$$

The condition that the surface of the spheroid is an equipotential gives the familiar condition

$$a^2a_0 = b^2\left(\beta_0 - \frac{\omega^2}{2\pi\rho}\right). \quad \dots (28)$$

Neglecting the variation of gravity for a small depth  $h$ , we may take the potential at the free surface

$$V = V_0 + gh, \quad \dots (29)$$

where 
$$g = \frac{\partial V}{\partial n}.$$

If  $l, m, n$  be the direction-cosines of the normal at  $x, y, z$

$$l = \frac{px}{a^2}, \quad m = \frac{py}{b^2}, \quad n = \frac{pz}{c^2},$$

$p$  being the perpendicular from the centre on the tangent surface.

Since the free surface must be an equipotential, we must have

$$gh=c \quad \dots (30)$$

But

$$ly=2\pi\rho a_0x \quad =\lambda\frac{x}{a^2},$$

$$my=2\pi\rho\left(\beta_0-\frac{\omega^2}{2\pi\rho}\right)y=\lambda\frac{y}{b^2},$$

$$nz=2\pi\rho\left(\beta_0-\frac{\omega^2}{2\pi\rho}\right)z=\lambda\frac{z}{b^2},$$

by virtue of equation (28),  $\lambda$  being a constant.

We have, therefore,

$$pg=\lambda,$$

and

$$h=kp, \quad \dots (31)$$

where  $k$  is a constant.

§ 9. The equation of the meridian section being

$$\frac{x^2}{c^2\xi^2} + \frac{\bar{\omega}^2}{c^2(1+\xi^2)} = 1$$

$$\frac{1}{p^2} = \frac{x^2}{c^2\xi^4} + \frac{\bar{\omega}^2}{c^2(1+\xi^2)^2} = \frac{\xi^2 + \bar{\xi}^2}{c^2\xi^2(1+\xi^2)}$$

and

$$\cos\theta = \frac{px}{c^2\xi^2} = \frac{\xi(1+\xi^2)^{1/2}}{(\xi^2 + \bar{\xi}^2)^{1/2}}.$$

The dynamical equations become (writing  $u$  for velocity in the direction of  $\xi$  and  $v$  for velocity in the direction of  $\phi$ )

$$\frac{\partial u}{\partial t} - 2\omega v \cos\theta = -h_1 \frac{\partial}{\partial \xi} (Z - \bar{Z})g$$

$$\frac{\partial v}{\partial t} + 2\omega u \cos\theta = -h_2 \frac{\partial}{\partial \phi} (Z - \bar{Z})g \quad \dots (32)$$

$Z$  being the equilibrium-height of the liquid.

The equation of continuity is

$$\frac{1}{h_1 h_s} \frac{dZ}{dt} = - \frac{\partial}{\partial \xi} \left( \frac{h_1 p}{h_s} \right) - \frac{\partial}{\partial \phi} \left( \frac{h_1 v}{h_s} \right). \quad \dots \quad (33)$$

For free oscillations, symmetrical about the axis,

$$\bar{Z}=0, \quad \frac{\partial Z}{\partial \phi}=0;$$

we have

$$\frac{\partial u}{\partial t} - 2\omega v \cos \theta = -h_1 \frac{\partial (Zg)}{\partial \xi},$$

$$\frac{\partial v}{\partial t} + 2\omega u \cos \theta = 0. \quad \dots \quad (34)$$

Eliminating  $v$ ,

$$\frac{\partial^2 u}{\partial t^2} + 4\omega^2 u \cos^2 \theta = -h_1 \frac{\partial^2 (Zg)}{\partial \xi \partial t^2}. \quad \dots \quad (35)$$

We have therefore as the Particular Integral, the exponential time factor  $e^{i\sigma t}$  being understood

$$u = \frac{h_1}{\sigma^2 - 4\omega^2 \cos^2 \theta} \frac{\partial^2 (Zg)}{\partial \xi \partial t^2}, \quad \dots \quad (36)$$

The complementary function is

$$u = A \cos (2\omega \cos \theta t + \epsilon). \quad \dots \quad (37)$$

Substituting in equation (33)

$$\frac{1}{h_s h_1} \frac{\partial Z}{\partial t} = -k \frac{\partial}{\partial \xi} \left( \frac{h_1 p}{h_s} \frac{\partial^2 (Zg)}{\partial \xi \partial t^2} \right).$$

Putting  $\eta$  for  $\frac{\partial Z}{\partial t}$ ,

$$\frac{\eta}{h_s h_1} = -k \frac{d}{d\xi} \left( \frac{h_1}{h_s} \cdot \frac{p}{\sigma^2 - 4\omega^2 \cos^2 \theta} \cdot \frac{d(g\eta)}{d\xi} \right). \quad \dots \quad (38)$$

Substituting for  $h_1$  and  $h_2$ , we get

$$c^2(\xi^2 + \zeta^2)^{\frac{1}{2}}(1 + \zeta^2)^{\frac{1}{2}}\eta = -k \frac{d}{d\xi} \left( \frac{c\xi(1 - \xi^2)(1 + \zeta^2)}{\xi^2 + \zeta^2} \frac{1}{\sigma^2 - 4\omega^2 \cos^2 \theta} \frac{d\eta}{d\xi} \right) \quad (39)$$

$\zeta$  being a constant  $a$  on the surface of the given spheroid. It is a linear differential equation of the second degree. The solution, however, is too complicated to admit physical interpretation.

§ 10. If we take the presence of the disturbing body into account, we have to substitute the value of  $\bar{Z}$ , which is the equilibrium-height. It is given by the value of the potential investigated in Art 7 above.

# ON A THEOREM OF LIE RELATING TO THE THEORY OF INTERMEDIATE INTEGRALS OF PARTIAL DIFFERENTIAL EQUATIONS OF THE SECOND ORDER

BY

HARENDRANATH DATTA

The theorem referred to is the following :—

*If a partial differential equation of the second order possesses two independent Intermediate Integrals (cf the Monge's type \*), it can be reduced to the form  $s=0$  by contact transformation.*

The object of the present paper is to show that the possession of two intermediate integrals is a *sufficient condition but not a necessary condition* for equations of the second order which can be transformed into the form  $s=0$  by contact transformation. For this purpose, it is enough to find at least one example in which the equation of the second order satisfies the following conditions :—

- I. It is reducible to the form  $s=0$ .
- II. The transformation used is a contact transformation.
- III. It does not possess two independent intermediate integrals of the Monge's type.

The equation found to satisfy the above conditions is the well-known equation of the Minimal surfaces, viz.,

$$(1+q^2)r-2pqs+(1+p^2)t=0.$$

## I

Taking Weierstrass's solution of the equation

$$(1+q^2)r-2pqs+(1+p^2)t=0, \quad \dots \quad (i)$$

we have

$$x=(1-u^2)U''+2uU'-2U+(1-v^2)V''+2vV'-2V \quad \dots \quad (ii)$$

$$y=i[-(1+u^2)U''+2uU'-2U+(1+v^2)V''-2vV'+2V] \quad (iii)$$

$$z=2uU''-2U'+2vV''-2V' \quad \dots \quad (iv)$$

\* From Art. 254, page 295 of Forsyth's *Theory of Differential Equations*, Vol. 6, it is clear that Integrals of Monge's type are meant here. The theorem was afterwards discovered independently by Darboux.



where  $U$  and  $V$  are arbitrary functions of  $u$  and  $v$  respectively and the dashes denote differentiations with respect to the corresponding parameter.

If, now, we choose co-ordinates  $X, Y, Z$  in such a way that  $X=u$ ,  $Y=v$  and  $Z=z$  [the relations between  $u, v$  and  $x, y$  being given by the equations (ii) and (iii)], then it is evident that (iv), when transformed, will reduce to  $\frac{\partial^2 Z}{\partial X \partial Y} = 0$  by differentiation.

But (iv) is really the most general solution (expressed in terms of  $X, Y, Z$ ) of the equation (i).

Hence, the differential equation (i) is *reducible to the form*  $s=0$  by the the preceding transformation.

## II

We find from (ii), (iii), (iv) and the relations  $X=u$ ,  $Y=v$ ,  $Z=z$  that

$$p = \frac{u+v}{1-uv}, \quad q = i \frac{u-v}{1-uv},$$

$$X = \frac{-i+i\sqrt{1+p^2+q^2}}{ip-q}, \quad Y = \frac{-i+i\sqrt{1+p^2+q^2}}{q+ip},$$

$$\frac{\partial X}{\partial p} = \frac{(1-uv)(1-u^2)}{2(1+uv)}, \quad \frac{\partial X}{\partial q} = i \frac{(1-uv)(1+u^2)}{2(1+uv)},$$

$$\frac{\partial Y}{\partial p} = \frac{(1-uv)(1-v^2)}{2(1+uv)}, \quad \frac{\partial Y}{\partial q} = i \frac{(1-uv)(1+v^2)}{2(1+uv)},$$

$$\frac{\partial Z}{\partial p} = \frac{1-uv}{1+uv} \{u(1-u^2)U''' + v(1-v^2)V'''\}$$

and 
$$\frac{\partial Z}{\partial q} = \frac{i(1-uv)}{1+uv} \{u(1+u^2)U''' + v(1+v^2)V'''\}.$$

Hence, 
$$P \equiv \frac{\partial Z}{\partial X} = 2uU'''$$

and 
$$Q \equiv \frac{\partial Z}{\partial Y} = 2vV'''.$$

Now, the transformation used will be a contact transformation if the relation

$$dZ - PdX - QdY = \rho(dz - pdr - qdy) \quad \dots \quad (v)$$

(where  $\rho$  does not vanish) is identically satisfied.

In the present case, the relation reduces to

$$PdX + QdY = pdr + qdy$$

if we take  $\rho = 1$ .

It is easy to see that this last relation is identically satisfied as each side of it becomes equal to

$$2uU''du + 2rV''dr$$

when expressed in terms of  $u$ ,  $r$ , etc.

Hence, the transformation used in reducing the equation (i) to the form  $s=0$  is a *contact transformation*, a fact which is at once clear from the consideration that both the sides of (v) are identically zero here.

### III

One of the subsidiary systems of equations (Boole's form) for the determination of the Intermediate integrals is the following :—

$$w_1 \equiv \frac{\partial w}{\partial q} - \rho_1 \frac{\partial w}{\partial p} = 0,$$

$$w_2 \equiv \frac{\partial w}{\partial x} + \sigma_1 \frac{\partial w}{\partial y} + (p + \sigma_1 q) \frac{\partial w}{\partial z} = 0,$$

$\rho_1$  and  $\sigma_1$  being respectively equal to

$$\frac{-pq + i\sqrt{1+p^2+q^2}}{1+q^2} \quad \text{and} \quad \frac{-pq - i\sqrt{1+p^2+q^2}}{1+q^2}$$

the roots of the equation

$$(1+q^2)\mu^2 + 2pq\mu + (1+p^2) = 0$$

If  $w_1$  and  $w_2$  co-exist, then

$$w'_2 \equiv w_2[w_1(w)] - w_1[w_2(w)] = 0$$

by virtue of  $w_1 = 0$  and  $w_2 = 0$ . This cannot be unless

$$w_2 \equiv \frac{\partial w}{\partial y} + k \frac{\partial w}{\partial z} = 0, \quad \text{where} \quad k = \frac{pq + i\sqrt{1+p^2+q^2}}{p - iq\sqrt{1+p^2+q^2}}.$$

Hence, we get  $w_3=0$  as a new equation. Now,  $(w_1, w_2)=0^*$  by virtue of  $w_3=0$ .

Also  $w_4 \equiv (w_2, w_3)=0$ .

But  $w'_3 \equiv (w_1, w_3) = \left( \rho \frac{\partial k}{\partial p} - \frac{\partial k}{\partial q} \right) \frac{\partial w}{\partial z}$ .

Hence  $w_5 \equiv \frac{\partial w}{\partial z} = 0$

is a new equation which is necessary to make  $w'_3=0$ .

We have now four equations, viz.,  $w_1=w_2=w_3=w_5=0$ , in five variables  $p, q, x, y, z$ . It is also easy to see that these four equations form a complete Jacobian system.

Hence, there can be only one integral common to  $w_1=0$  and  $w_2=0$ .

Hence, there is no Intermediate Integral (involving an arbitrary function) of the Monge's type. Similarly, it can be seen that the other system does not possess any such Integral.

Hence, we conclude that the possession of two Intermediate Integrals is a *sufficient condition but not a necessary condition* for equations of the second order which can be transformed into the form  $s=0$  by contact transformation.

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\* The notations are the same as those used in Forsyth's *Theory of Differential Equations*.

# ON AN EXPRESSION FOR $\frac{d}{dn} J_n(x)$

BY

SUBODCHANDRA MITRA

The object of the present note is to find a proof for a known expression for  $\frac{d}{dn} J_n(x)$ .

It is possible for us to express  $\frac{d}{dn} J_n(x)$  in the form

$$\begin{aligned} \frac{d}{dn} J_n(x) = & J_n(x) \log x - \left( \log 2 + \frac{\Gamma'(n+1)}{\Gamma(n+1)} \right) J_n(x) \\ & + \left\{ \frac{(n+2)}{(n+1)} J_{n+2}(x) - \frac{(n+1)}{2(n+2)} J_{n+1}(x) + \frac{(n+6)}{3(n+3)} J_{n+3}(x) \right. \\ & \left. - \dots + (-1)^{r-1} \frac{(n+2r)}{r(n+r)} J_{n+2r}(x) + \dots \right\} \end{aligned}$$

$J_n(x)$  satisfies the differential equation

$$\frac{d^2 J_n(x)}{dx^2} + \frac{1}{x} \frac{dJ_n(x)}{dx} + \left( 1 - \frac{n^2}{x^2} \right) J_n(x) = 0.$$

Differentiating with respect to  $n$  and writing

$$v = \frac{dJ_n(x)}{dn},$$

we have

$$\frac{d^2 v}{dx^2} + \frac{1}{x} \frac{dv}{dx} + \left( 1 - \frac{n^2}{x^2} \right) v = \frac{2n}{x^2} J_n(x). \quad \dots \quad (A)$$

To find a solution of (A) we write

$$\begin{aligned} v = & J_n(x) \log x + \{ A_n J_n(x) + A_{n+2} J_{n+2}(x) + A_{n+4} J_{n+4}(x) \\ & + A_{n+6} J_{n+6}(x) + \dots + A_{n+2r} J_{n+2r}(x) + \dots \} \end{aligned}$$

Substituting for  $v$  in (A) and taking account of the differential equations satisfied by  $J_n(x)$ ,  $J_{n+2}(x)$ , etc., we have after a little simplification,

$$\begin{aligned} A_{n+1} \left\{ \frac{(n+2)^2 - n^2}{x^2} \right\} J_{n+2}(x) + A_{n+3} \left\{ \frac{(n+4)^2 - n^2}{x^2} \right\} J_{n+4}(x) \\ + \dots + A_{n+2r} \left\{ \frac{(n+2r)^2 - n^2}{x^2} \right\} J_{n+2r}(x) + \dots \\ = \frac{2n}{x^2} J_n(x) - \frac{2}{x} J'_n(x). \end{aligned} \quad \dots \quad (B)$$

Making use of the recurrence formula,

$$J'_n(x) = J_{n-1}(x) - \frac{n}{x} J_n(x),$$

we have

$$\begin{aligned} A_{n+2} \{(n+2)^2 - n^2\} J_{n+2}(x) + A_{n+4} \{(n+4)^2 - n^2\} J_{n+4}(x) + \dots \\ + A_{n+2r} \{(n+2r)^2 - n^2\} J_{n+2r}(x) + \dots \\ = 4n J_n(x) - 2x J_{n-1}(x). \end{aligned}$$

Now

$$x J_{n-1}(x) = 2n J_n(x) - 2(n+2) J_{n+2}(x) + 2(n+4) J_{n+4}(x) - \dots$$

Therefore

$$\begin{aligned} A_{n+2} \{(n+2)^2 - n^2\} J_{n+2}(x) + A_{n+4} \{(n+4)^2 - n^2\} J_{n+4}(x) + \dots \\ + A_{n+2r} \{(n+2r)^2 - n^2\} J_{n+2r}(x) + \dots \\ = 4(n+2) J_{n+2}(x) - 4(n+4) J_{n+4}(x) + 4(n+6) J_{n+6}(x) - \dots \\ + (-)^{r-1} 4(n+2r) J_{n+2r}(x) + \dots \end{aligned} \quad \dots \quad (C)$$

Therefore equating the co-efficients, we have,

$$\begin{aligned} A_{n+2} &= \frac{(n+2)}{(n+1)}, & A_{n+4} &= + \frac{(n+4)}{2(n+2)}, \\ &\dots & \dots & \dots \\ A_{n+2r} &= (-)^{r-1} \frac{(n+2r)}{r(n+r)}. \end{aligned}$$

It now remains to determine  $A_n$ . When  $n$  is any number, real or complex

$$J_n(x) = \frac{x^n}{2^n \Gamma(n+1)} \left\{ 1 - \frac{x^2}{2^2 1! (n+1)} + \frac{x^4}{2^4 2! (n+1)(n+2)} - \dots \right\}$$

the expression being rendered precise by taking for  $x$  its principal value.

Therefore the co-efficient of  $x$  in  $\frac{d}{dn} J_n(x)$  is

$$-\left( \frac{\log 2}{2^n \Gamma(n+1)} + \frac{\Gamma'(n+1)}{2^n \{\Gamma(n+1)\}^2} \right)$$

and equating it to the co-efficient of  $x^n$  in  $A_n J_n(x)$ , we have

$$A_n = -\left( \log 2 + \frac{\Gamma'(n+1)}{\Gamma(n+1)} \right).$$

In conclusion I wish to express my indebtedness to Dr. N. M. Basu for the interest he always takes in my work and to Dr. A. B. Datta for his kind revision and expression of opinion.

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# A FEW INTERESTING RESULTS IN CONNECTION WITH THE MOTION OF A HEAVY INEXTENSIBLE CHAIN OVER A FIXED VERTICAL PULLEY

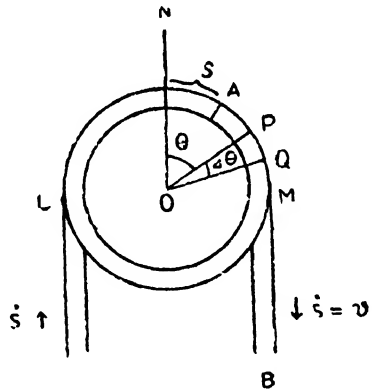
BY  
A. C. BANERJI.

§ 1. Let us first assume that there is no friction between the chain and the pulley, and the resistance of the air is neglected, and the cross section of the chain is small.

It will be an interesting exercise first to find the difference between the tensions at any instant at the two points L, M, where the chain ceases to be in contact with the pulley.

Let  $a$  be the radius of the pulley, and let  $m$  be the linear density of the chain which is supposed to be constant; let A be a marked point on the chain; let the arc NA be  $s$  at the instant  $t$ ; let P be any other point on the chain and let the length AP be  $\sigma$ ; let the element PQ of the chain be  $\Delta\sigma$ ; let  $\angle NOP$  be  $\theta$  and  $\angle POQ$  be  $\Delta\theta$ .

Let R be the reaction per unit length between the pulley and the chain at the point P at the instant  $t$ .



The total reaction on PQ is  $R\Delta\sigma$  to the first order of small quantities along a direction making an angle  $\Delta\phi$  with OP where  $\Delta\phi < \Delta\theta$ .

Consider the equation of motion for the element PQ of the chain along the tangent at P.

Each element of the chain has the same velocity and acceleration as the marked point A at any instant

$$m\Delta\sigma\dot{v} = m\Delta\sigma g \sin \theta + (T + \Delta T) \cos \Delta\theta - T + R\Delta\sigma \sin \Delta\phi;$$

neglecting small quantities of 2nd order we have,

$$m\Delta\sigma\dot{v} = m\Delta\sigma g \sin \theta + \Delta T.$$



Dividing by  $\Delta\sigma$  and proceeding to limit we have,

$$m\dot{v} = mg \sin \theta + \frac{dT}{d\sigma} \quad \dots (A)$$

Now again,

$$a\theta = s + \sigma,$$

as  $s$  is independent of  $\sigma$ , differentiating along the chain we get

$$a d\theta = d\sigma.$$

Integrate (A) with respect to  $\sigma$  from L to M and let  $T_1$  and  $T_2$  be the tensions at L and M respectively ; we have

$$mv \int_L^M d\sigma = mg \int_L^M \sin \theta d\sigma + \int_L^M dT,$$

$$m\dot{v}\pi a = mga \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \sin \theta d\theta + T_2 - T_1$$

$$\therefore m\pi a\dot{v} = T_2 - T_1. \quad \dots (B)$$

Let us examine this equation. There are three interesting cases here.

$$(i) \quad T_2 \longrightarrow T_1, \quad \text{when } m \longrightarrow 0;$$

i.e., the two tensions are the same if the chain is light.

$$(ii) \quad T_2 \longrightarrow T_1, \quad \text{when } a \longrightarrow 0;$$

i.e., the two tensions are the same if the pulley is small even if the chain is not light.

$$(iii) \quad T_2 = T_1, \quad \text{when } \dot{v} = 0;$$

i.e. the two tensions are the same if the chain is moving with uniform speed even if the chain is not light and the pulley is not small.

Let us now calculate the total vertical upward pressures on chain.

It is

$$\int_L^M R d\sigma \cos \theta$$

Now the equation of motion of the element PQ of chain along the inward normal at P is

$$m \Delta \sigma \frac{v^2}{a} = m \Delta \sigma g \cos \theta - R \Delta \sigma \cos \Delta \phi + (T + \Delta T) \sin \Delta \theta ;$$

neglecting small quantities of the 2nd order we have

$$\begin{aligned} \frac{mv^2}{a} \Delta \sigma &= m \Delta \sigma g \cos \theta - R \Delta \sigma + T \Delta \theta \\ &= m \Delta \sigma g \cos \theta - R \Delta \sigma + \frac{T}{a} \Delta \sigma \end{aligned}$$

$$\therefore R = -\frac{mv^2}{a} + mg \cos \theta + \frac{T}{a},$$

where T is the tension at P

§ 2. Now let us find out T.

Integrate equation (A) with respect to  $\sigma$  from L to P ; we have,

$$\begin{aligned} mv \int_L^P d\sigma &= mg \int_L^P \sin \theta d\sigma + \int_L^P dT \\ mv \left( \frac{a\pi}{2} + a\theta \right) &= mga \int_{-\frac{\pi}{2}}^{\theta} \sin \theta d\theta + T - T_1 \\ &= -mga \cos \theta + T - T_1 \end{aligned}$$

$$\therefore T = T_1 + mva \left( \frac{\pi}{2} + \theta \right) + mga \cos \theta ;$$

$$\therefore R = -\frac{mv^2}{a} + 2mg \cos \theta + \frac{T_1}{a} + mv \left( \frac{\pi}{2} + \theta \right). \quad \dots \quad (C)$$

Now let the total vertical Thrust on the chain be  $F$ . Then

$$\begin{aligned}
 F &= \int_L^M R d\sigma \cos \theta = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} R a d\theta \cos \theta \\
 &= \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} a d\theta \cos \theta \left\{ \frac{T_1 - mv^2}{a} + m\dot{v} \left( \frac{\pi}{2} + \theta \right) + 2mg \cos \theta \right\} \\
 &= 2(T_1 - mv^2) + m a v \pi + m g a \pi \quad \dots (D) \\
 &= T_1 + T_2 - 2mv^2 + m g a \pi \quad \dots (E)
 \end{aligned}$$

as

$$T_2 = T_1 + m a v \pi$$

Let us also examine this equation ; there are three interesting cases :

(i) Let  $m \longrightarrow 0$ , then  $F \longrightarrow 2T_1$ ,

from (D), i.e., if the chain be light then the total vertical thrust on the chain is twice the tension at  $L$  or  $M$ .

(ii) Let  $v = 0$  and  $\dot{v} = 0$ , then  $F = 2T_1 + m g a \pi$

i.e., if the chain is at rest and continues to be at rest then the total vertical thrust on the chain is twice the tension at  $L$  or  $M$  together with the weight of the chain in contact with the pulley.

[N.B.—If initially  $v = 0$ , but  $\dot{v} \neq 0$ , then

$$F = T_1 + T_2 + m g a \pi$$

from (E), here

$$T_2 \neq T_1$$

i.e., if the chain initially starts from rest, then the tensions at  $L$  and  $M$  are different, and the total vertical thrust at that instant on the chain is equal to the sum of the tensions at  $L$  and  $M$ , together with the weight of the chain in contact with the pulley.]

(iii) Let  $a \longrightarrow 0$  then  $F \longrightarrow 2(T_1 - mv^2)$  ;

i.e., if the pulley is small, the total vertical thrust on the chain is less than twice the tensions at  $L$  or  $M$  by  $2mv^2$ .

§ 3. Let us now consider in the case of a large smooth pulley, if it is possible to make the total vertical thrust between the chain and the pulley vanish.

Let the end B of the chain be free. Let us consider the equation of motion of the portion BM of the chain and let  $x$  be measured from M ;

$$\therefore mrv \frac{dv}{dx} = mgx - T_2.$$

We have also

$$T_2 = T_1 + m\dot{v}\pi ;$$

$$\therefore mrv \frac{dv}{dx} = mgx - T_1 - m\dot{v}\pi$$

$$\therefore T_1 = -mrv \frac{dv}{dx} + mgx - m\dot{v}\pi.$$

Now the total thrust vanishes when  $F=0$

$$i.e. \quad 2(T_1 - mv^2) + m\dot{v}\pi + mga\pi = 0$$

from (D)

$$\therefore -2rv \frac{dv}{dx} + 2gx - 2\dot{v}\pi - 2v^2 + \dot{v}\pi + ag\pi = 0,$$

Now as

$$\dot{v} = v \frac{dv}{dx},$$

we have

$$(2x + a\pi)v \frac{dv}{dx} + 2v^2 = 2g \left( x + \frac{a\pi}{2} \right). \quad \dots (G)$$

$$\text{Put } x + \frac{a\pi}{2} = z; \quad \text{then } v \frac{dv}{dz} + v^2 = gz$$

$$\therefore \frac{d}{dz}(z^2 v^2) = 2gz^2$$

or

$$z^2 v^2 = \frac{2gz^3}{3} + \text{const.}$$

If we have the initial conditions that  $v = \sqrt{\frac{ag\pi}{3}}$ , when  $z = \frac{a\pi}{2}$   
i.e.,  $x=0$ , we find the constant to be zero.

§ 4. It is *experimentally* possible to have these initial conditions.

At first we can hold the chain at rest with free end B at M by means of some contrivance applied to the left hand portion of the chain.

Then as soon as the experiment begins, we apply a suitable impulse at B so that a velocity equal to  $\sqrt{\frac{ag\pi}{3}}$  is imparted to the chain, and at the same time the contrivance is let go.

If it is objected, that with free end B at M, it is not easy to apply a contrivance to the left hand portion of the chain, before the experiment begins, we can alter these initial conditions a bit and get new initial conditions which will also make the constant zero.

Initially take BM or  $x$  to be  $\frac{a\pi}{2}$ . At first we attach a clip fixed to a stand to the portion BM, and another clip fixed also to a stand is attached to the left hand portion of the chain. As soon as the experiment begins we apply a suitable impulse at B imparting a velocity  $\sqrt{\frac{2ga\pi}{3}}$  to the chain and at the same instant two clips are let go.

Under these initial conditions we have the constant zero ;

$$\therefore v^2 = \frac{2}{3}gz = \frac{2}{3}g\left(x + \frac{a\pi}{2}\right)$$

$$\therefore v \frac{dv}{dt} = \frac{g}{3}x = \frac{g}{3}v$$

$$\therefore \frac{dv}{dt} = \frac{g}{3}$$

This is an interesting and important result. In the case of a large smooth pulley, the vertical thrust between the chain with a free end B and the pulley will vanish if the chain moves with an acceleration equal to one third of gravity, with the initial condition as if a velocity equal to  $\sqrt{\frac{ag\pi}{3}}$  is imparted to the chain when the free end B is at M i.e. at the same level with the centre of the pulley.

When the radius of the pulley tends to zero, this initial velocity tends to zero. So in the case of a very small pulley we can say without much error that the initial conditions are  $v=0$ , when  $x=0$ .

By suitable arrangements on the left hand portion of the chain it is *experimentally* possible to make the chain move with an acceleration equal to one third of gravity.

§ 5. Now let us take the case when a weight equal to that of length “ $l$ ” of the chain is attached to the free end B of the chain.

The equation of motion for the portion BM of the chain with the weight attached at B, becomes

$$m(x+l)v\frac{dv}{dx}=mg'(x+l)-T_1,$$

and equation (G) becomes

$$(2x+2l+a\pi)v\frac{dv}{dz}+2v^2=2g\left(x+l+\frac{a\pi}{2}\right).$$

$$\text{Put } z=x+l+\frac{a\pi}{2},$$

then we have

$$v\frac{dv}{dz}+v^2=gz$$

$$\therefore z^2v^2=\frac{2gz^3}{3}+\text{const}$$

If we have the initial conditions such that

$$v=\sqrt{\frac{g}{3}(a\pi+2l)}$$

$$\text{when } z=l+\frac{a\pi}{2}, \quad \text{i.e., } x=0;$$

we have the constant equal to zero.

$$\therefore v^2=\frac{2gz}{3}=\frac{2g}{3}\left(x+l+\frac{a\pi}{2}\right).$$

$$\therefore \frac{dv}{dt}=\frac{1}{2}g.$$

In the case where a weight equal to that of length  $l$  of the chain is attached to the free end B, the vertical thrust between the chain and the pulley will vanish if the chain moves with an acceleration equal to one third of gravity, with the initial condition as if a velocity equal

to  $\sqrt{\frac{g}{3}(\pi + 2l)}$  is imparted to the chain when the free end B is at M, i.e., at the same level with the centre of the pulley.

§ 6. Let us now consider the total horizontal thrust on the chain. Let H be the total horizontal thrust. Then

$$\begin{aligned} H &= \int_L^M R d\sigma \sin \theta = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} R a d\theta \sin \theta \\ &= \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} a \sin \theta \left\{ \frac{T_1 - mv^2}{a} + m\dot{v} \left( \frac{\pi}{2} + \theta \right) + 2mg \cos \theta \right\} d\theta \\ &= 2ma\dot{v} \end{aligned}$$

Now let us examine the three cases :—

(i) When  $m \rightarrow 0$ ,  $H \rightarrow 0$  ;

i.e., when the chain is light, the total horizontal thrust vanishes even if the pulley be not small.

(ii) When  $a \rightarrow 0$ ,  $H \rightarrow 0$  ;

i.e. when the pulley is small, the total horizontal thrust vanishes even if the chain be not light

(iii) When  $v = 0$ ,  $H \rightarrow 0$  ;

i.e., when the chain moves with uniform speed the total horizontal thrust vanishes.

[N.B. By means of suitable arrangements it is not impossible to make the chain move with uniform speed.]

# NEW METHODS OF APPROXIMATING TO THE ROOTS OF A NUMERICAL EQUATION

BY

NRIPENDRANATH GHOSH

The object of this paper is to develop a new method and to indicate others by which the solution of any numerical equation can be approximated to. The procedure adopted embraces some methods already known and of these methods special interest has been attached in this paper to those of Newton, Horner and McClintock. It will appear in course of development that certain improvements have been made or attempted with regard to each of the above-mentioned methods.

## *The underlying principle*

1. We shall consider for simplicity of treatment rational integral numerical equations. Let  $\phi(z)=p$  be such an equation of degree  $n$ . Let there be a root differing by a small quantity from a number  $a$ . We shall describe methods by which the required root may be calculated to any desired degree of approximation.

Denoting by  $x$  the number  $p-\phi(a)$ , the above equation can be put in the form  $\phi(z)=\phi(a)+x$ , where we call  $x$  the *residue* of the equation corresponding to  $a$ . The ultimate process of obtaining the root depends now upon the following fundamental theorem :—

If  $a_0, a_1, a_2, \dots, a_s$  and  $\xi$  be arbitrary parameters there exists a rational integral identity

$$\phi(a_0 + a_1\xi + a_2\xi^2 + \dots + a_s\xi^s) = A_0 + A_1\xi + A_2\xi^2 + \dots + A_{s+s}\xi^{s+s} \dots \quad (A)$$

where  $A_0, A_1, A_2, \dots$  are known rational integral functions of  $a_0, a_1, a_2, \dots$  given by

$$A_0 = \phi(a_0)$$

$$A_1 = a_1\phi'(a_0)$$

$$2A_2 = a_1^2\phi''(a_0) + 2a_2\phi'(a_0)$$

$$3A_3 = a_1^3\phi'''(a_0) + 6a_1a_2\phi''(a_0) + 6a_3\phi'(a_0)$$





*Horner's Method*

3. The method due to Horner of solving numerical equations is one of these where the above principle is maintained. Before passing on to indicate other methods we wish to consider this straight-forward one with special reference to the particular mode in which the expression  $u_A$  is made to approach  $\phi(a)+x$ . Avoiding details of the process, as being unnecessary here, we may proceed thus :

The first trial  $a$ , having been made with regard to the required root of the equation  $\phi(z)=p$ , we have

$$\phi(a)+x=p \quad \dots (i)$$

Put then  $a_0=a$  in the identity (A) and consider the collection of terms of the expression  $u_A$  represented by  $\phi(a+a_1\xi)-\phi(a)$ . Form the equation  $\phi(a+a_1\xi)-\phi(a)=x$  and let  $a_1x$  be an approximate value of  $a_1\xi$  (found by suitable trials) of the above equation, so that

$$\phi(a+a_1x)-\phi(a)=x-r_1, \quad \text{where } |x_1| < |x| \quad \dots (ii)$$

Put then  $a_1\xi=a_1x$  in the identity (A) and consider the terms of  $u_A$  contained in the next collection  $\phi(a+a_1x+a_2\xi^2)-\phi(a+a_1x)$ . Form the equation  $\phi(a+a_1x+a_2\xi^2)-\phi(a+a_1x)=x_1$  and let  $a_2x^2$  be an approximate value of  $a_2\xi^2$  (found as before by trials) in this equation, so that

$$\phi(a+a_1x+a_2x^2)-\phi(a+a_1x)=x_1-r_2, \quad \text{where } |x_2| < |x_1| \quad (iii)$$

Put then  $a_2\xi^2=a_2x^2$  in the identity (A) and proceed as before. The  $(s+1)$ th relation thus obtained will be

$$\begin{aligned} \phi(a+a_1x+a_2x^2+\dots+a_sx^s)-\phi(a+a_1x+a_2x^2+\dots+a_{s-1}x^{s-1}) \\ =x_{s-1}-r_s, \quad \text{where } |x_s| < |x_{s-1}| \dots (s+i) \end{aligned}$$

Combining the relations (i), (ii), (iii) ... (s+i) we have

$$\phi(a+a_1x+a_2x^2+\dots+a_sx^s)=p-r_s$$

where  $x_s$  represents the *residue* corresponding to

$$a+a_1x+a_2x^2+\dots+a_sx^s$$

Since  $|x|, |x_1|, |x_2| \dots |x_s|$  form a sequence of decreasing numbers, the approach of  $u_A$  towards  $\phi(a)+x$ , i.e.,  $p$  is definite and certain.

4. The successive collections of terms in  $u_A$  associated with the above process mark the path of approach of  $u_A$  towards  $\phi(a)+x$ . The manner of collecting resorted to in Horner's method is exhaustive; for in considering a certain collection say...

$$\phi(a+a_1x+a_2x^2+a_3x^3)-\phi(a+a_1x+a_2x^2)$$

of  $u_A$  we notice that all the terms involving the unknown  $a_3x^3$  are included. Such collections from  $u_A$  will be called *complete* while others containing lesser number of terms involving the unknown will be called *partial*. A partial collection having a single term involving the unknown is said to be *simple*, otherwise it is called *multiple*. The collections represented by  $A_1\xi, A_2\xi^2, A_3\xi^3 \dots$  involving respectively the unknowns  $a_1\xi, a_2\xi^2, a_3\xi^3 \dots$  are all *simple partial collections*. Since they present themselves naturally in the formation of the identity (A) we shall call these the *natural system of partial collections*.

### A New Method by Series

5. Proceeding in succession along this natural system of collections we develop a new method of solving numerical equations by means of series in the following way :—

Put  $a_0=a$  in the identity (A) and consider the collection  $A_1\xi$ . Form the equation  $A_1\xi=x$  linear in  $a_1\xi$ ; whence  $a_1\xi=\frac{x}{\phi'(a)}$  (provided  $\phi'(a)\neq 0$ ). Put then  $a_1\xi=\frac{x^2}{\phi'(a)^2}$  in the identity (A) and consider the next collection  $A_2\xi^2$ . Form the equation  $A_2\xi^2=0$  linear in  $a_2\xi^2$ ; whence

$$a_2\xi^2=-\frac{x^2}{2} \cdot \frac{\phi''(a)}{\{\phi'(a)\}^3}.$$

Substitute this value of  $a_2\xi^2$  in the identity (A) and form the next equation  $A_3\xi^3=0$ ; whence

$$a_3\xi^3=\frac{x^3}{3} \cdot \frac{3\{\phi''(a)\}^2-\phi'(a)\phi'''(a)}{\{\phi'(a)\}^5}$$

Continuing in this manner we come upon the collection represented by  $A_s \xi^s$ , whence we choose  $a_s \xi^s$  such that  $A_s \xi^s = 0$ , the group of terms

$$-(A_{s+1} \xi^{s+1} + A_{s+2} \xi^{s+2} + \dots + A_{\infty} \xi^{\infty})$$

representing the corresponding residue. So long as the residues tend to become numerically smaller and smaller as  $s$  increases, the required root is given more and more accurately by the  $(s+1)$  terms of the infinite series

$$a + \frac{x}{\phi'(a)} - \frac{x^2}{2} \cdot \frac{\phi''(a)}{\{\phi'(a)\}^3} + \frac{x^3}{3} \cdot \frac{3\{\phi''(a)\}^2 - \phi'(a)\phi'''(a)}{\{\phi'(a)\}^5} - \dots$$

If  $C_r$  and  $C_{r+1}$  be the co-efficients of  $\frac{x^r}{r}$  and  $\frac{x^{r+1}}{r+1}$  respectively in this

series then it will be found that

$$\left( \frac{1}{\phi'(a)} \frac{d}{da} \right) C_r = C_{r+1}$$

We shall represent the above series by the symbol  ${}^x\rho_\phi$  or simply by  $\rho$  and the value calculated up to its  $(s+1)$ th term by  $a_s$ . Let  $R_s$  denote the residue corresponding to  $a_s$ ; then we have the obvious relation  $\phi(a_s) + R_s = \phi(a) + x$ .

#### *Newton's Method*

6. Sometimes it is convenient to have the equation in the form  $\phi(x)=0$ . To find the required root we put  $x=-\phi(a)$  in the series  ${}^x\rho_\phi$  and obtain the following series

$$a - \frac{\phi(a)}{\phi'(a)} - \frac{\{\phi(a)\}^2}{2} \cdot \frac{\phi''(a)}{\{\phi'(a)\}^3} \\ - \frac{\{\phi(a)\}^3}{3} \cdot \frac{3\{\phi''(a)\}^2 - \phi'(a)\phi'''(a)}{\{\phi'(a)\}^5} - \dots$$

represented by  $-\phi_\rho$ .

If we take only the first two terms of the series  $-\phi_{\rho\phi}$  then by the process of iteration there follows the method of solving an equation of the form  $\phi(z)=0$  due to Newton. Since now we have found the complete series  $-\phi_{\rho\phi}$  we may apply the process of iteration beyond the second term. If, however, the series  $-\phi_{\rho\phi}$  be not slowly convergent the process of iteration may with advantage be altogether dispensed with.

7. Let us illustrate the application of the series  ${}^x\rho\phi$  or  $-\phi_{\rho\phi}$  by considering the following examples :—

*Ex. (i)* Solve  $z^3 - 2z - 5 = 0$ .

Suppose we are going to find the root lying between 2 and 3.

Put the equation in the form  $\phi(z)=p$ , so that  $\phi(z)=z^3-2z$  and  $p=5$  choose  $a=2$ , then  $\phi(a)=4$  and  $p-\phi(a)=1$ .

$$\text{Also} \quad \phi'(a)=10,$$

$$\phi''(a)=12,$$

$$\phi'''(a)=6,$$

$$\phi^{(4)}(a)=0$$

Substituting these values in the series  ${}^x\rho\phi$  we have

$$\begin{aligned} a_3 &= 2 + \frac{1}{10} - \frac{1}{2} \cdot \frac{12}{10^2} + \frac{1}{3} \cdot \frac{3 \cdot 12^2 - 10 \cdot 6}{10^3} \\ &= 2 + \cdot 1 - \cdot 006 + \cdot 00062 \\ &= 2 \cdot 09462, \end{aligned}$$

which gives the root correct to the third decimal figure. Proceeding to  $a_4, a_5, a_6, \dots$  we get more and more accurate values. For a closer choice 2.1 of  $a$ , even  $a_3$  gives the root correct to the 7th or 8th figure.

Ex. (ii) Solve  $z^4 + 4z^3 - 4z^2 - 11z + 4 = 0$ .

Let us find the root lying between 1 and 2.

Take  $\phi(z) = z^4 + 4z^3 - 4z^2 - 11z + 4,$

then  $\phi'(z) = 4z^3 + 12z^2 - 8z - 11,$

$$\phi''(z) = 12z^2 + 24z - 8,$$

$$\phi'''(z) = 24z + 24,$$

$$\phi^{(4)}(z) = 24,$$

and the equation has the form  $\phi(z) = 0$ .

(a) Choose  $a=1$ , then

$$\phi(a) = -6, \quad \phi'(a) = -3, \quad \phi''(a) = 28,$$

$$\phi'''(a) = 48, \quad \phi^{(4)}(a) = 24.$$

The ratio  $\frac{\phi(a)}{\phi'(a)}$  being greater than 1, the series  $-\phi_{\rho\phi}$  obviously cannot afford a root.

(b) Choose  $a=2$ , then

$$\phi(a) = 14, \quad \phi'(a) = 53, \quad \phi''(a) = 88,$$

$$\phi'''(a) = 72, \quad \phi^{(4)}(a) = 24.$$

Substituting these values in  $-\phi_{\rho\phi}$  we have

$$\begin{aligned} a_s &= 2 - \frac{14}{53} - \frac{14^2}{2 \cdot 53^2} - \frac{88}{3 \cdot 53^3} - \frac{14^3}{3 \cdot 53^4} - \frac{3 \cdot 88^2 - 53 \cdot 72}{(53)^5} \\ &= 2 - .264151 - .057927 - .021233 \\ &= 1.65\dots, \end{aligned}$$

where we can scarcely depend upon its first decimal figure, the series being slowly convergent. We, however, see that 1.6 is a closer choice for  $a$  than 2.

In numerical calculations logarithmic tables have been used.

(c) When  $a=1.6$

$$\phi(a) = -.9024, \quad \phi'(a) = 23.304, \quad \phi''(a) = 61.12,$$

$$\phi'''(a) = 62.4, \quad \phi^{(4)}(a) = 24.$$

Now  $a_s$  becomes

$$1.6 - \frac{.9024}{23.304} - \frac{(.9024)^2}{12} \cdot \frac{61.12}{(23.304)^2} \\ + \frac{(.9024)^3}{13} \cdot \frac{3(61.12)^2 - 23.304 \times 62.4}{(23.304)^3}$$

$$\text{or} \quad 1.6 + .038723 - .0019663 + .0001738,$$

$$\text{or} \quad 1.63693,$$

which gives the root correct even up to the fourth decimal figure.

In order that the series  ${}^w\rho_\phi$  or  $-{}^w\rho_\phi$  (as the case may be) may afford a root it is essential that the series must not be slowly convergent. The values of  $a$  for which this is maintained are in general ranged within limits either wide or narrow. For want of a *simple convergency-criterion* of the above series these limits cannot be definitely pre-assigned.

8. Referring to Art. 5 we observe that the series  ${}^w\rho_\phi$  was formed under the tacit assumption that  $A_1\xi$  is numerically the greatest collection in  $u_A$ . If  $|a_1\xi|$  is sufficiently small it is in general so irrespective of

the values of  $\phi'(a)$ ,  $\phi''(a)$ ,  $\phi'''(a)\dots$ \* Since  $a_1\xi = \frac{x}{\phi'(a)}$  it follows

that  $|x|$  should be sufficiently small. Thus the series  ${}^w\rho_\phi$  must lead to a root provided  $a$  can be so chosen that the residue corresponding to it is sufficiently small in numerical value.

If  $|a_1\xi|$  is only less than 1, but not sufficiently small, unless  $\phi'(a)$  happens to be large enough we cannot expect  $A_1\xi$  to be the greatest collection. The term  $\frac{(a_1\xi)^2}{12} \phi''(a)$ , for instance may exceed  $A_1\xi$  in

\*  $|a_1\xi|$ ,  $|a_2\xi^2|$ ,  $|a_3\xi^3| \dots$  necessarily forming a sequence of decreasing numbers.

numerical value if  $|\phi'(a)|$  tend to become small while  $|\phi''(a)|$  tend to increase. The series  ${}^{\rho}\phi$  will fail in a case like this. A different mode of collecting the terms of  $u_A$  yields, however, an auxiliary series applicable in such a case. We shall describe the method in the next article.

Returning for a moment to Horner's method it may be remarked that the series  ${}^{-\phi}\rho_{\phi}$  can be applied at some stage in the method to reduce the labour entailed in the process. The chief labour consists in the calculation of  $r$ 's at successive stages of the method and it must be remembered that these calculations are intimately related with the process. In practice, the application of the series  ${}^{-\phi}\rho_{\phi}$  is most convenient when the *trial divisor* is effective (that is the residue is *sufficiently* small).

#### *Case of failure of the series $\rho$*

9. Let us first explain the particular mode of collecting terms required in this process. Take the term  $\frac{(a_1\xi)^2}{2}\phi''(a_0)$  in  $A_2\xi^2$  and form the first collection  $K_1$ . Next take the term  $A_1\xi$  along with all but the last in  $A_2\xi^2$  and form the second collection  $K_2$ . Thus  $K_2$  will consist of the terms

$$a_1\xi\phi'(a_0) + \frac{(a_1\xi)^3}{3}\phi'''(a_0) + a_1\xi a_2\xi^2\phi''(a_0).$$

Next take the last term in  $A_2\xi^2$  along with all but the last in  $A_3\xi^3$  and form the third collection  $K_3$ . Finally the  $s$ th collection  $K_s$  will involve the last term in  $A_{s-1}\xi^{s-1}$  together with all the terms in  $A_{s+1}\xi^{s+1}$ . The successive partial collections thus formed are all simple.

Put then  $a_0 = a$  in the identity (A) and choose  $a_1\xi, a_2\xi^2, a_3\xi^3 \dots a_s\xi^s$  such that  $K_1 = 0, K_2 = 0, K_3 = 0, \dots, K_s = 0$ ; we then have

$$\begin{aligned} & \phi(a_0 + a_1\xi + a_2\xi^2 + \dots + a_s\xi^s) \\ &= \phi(a) + x + a_s\xi^s\phi'(a) + A_{s+1}\xi^{s+1} + A_{s+2}\xi^{s+2} + \dots + A_{s+n}\xi^{s+n} \end{aligned}$$



where  $a_0 = a$ ,

$$a_1 \xi = \pm \left\{ \frac{2x}{\phi''(a)} \right\}^{\frac{1}{2}},$$

$$a_2 \xi^2 = -\frac{\phi'(a)}{\phi''(a)} - \frac{1}{3} \cdot \frac{\phi'''(a)}{\{\phi''(a)\}^2},$$

$$a_3 \xi^3 = \pm \left\{ \frac{\phi''(a)}{2x} \right\}^{\frac{1}{2}} \left[ \frac{1}{2} \frac{\{\phi'(a)\}^2}{\{\phi''(a)\}^3} + \frac{x\phi'(a)\phi'''(a)}{\{\phi''(a)\}^3} \right. \\ \left. - \frac{1}{6} \frac{x^2 \phi^{(4)}(a)}{\{\phi''(a)\}^3} + \frac{5}{18} \frac{x^2 \{\phi'''(a)\}^2}{\{\phi''(a)\}^4} \right];$$

and so on.

The process of inversion may thus be performed in two ways under the tacit assumption that  $K_1$  is numerically the greatest collection among the  $K$ 's. So long as the residue

$$-\{a_s \xi^s \phi'(a) + A_{s+1} \xi^{s+1} + \dots + A_{s+n} \xi^{s+n}\}$$

tends in each case to become smaller and smaller in numerical value as  $s$  increases, a pair of roots of the equation  $\phi(z) = \phi(a) + x$  is given more and more accurately by the  $(s+1)$  terms of the infinite-series

$$a \pm \left\{ \frac{2x}{\phi''(a)} \right\}^{\frac{1}{2}} - \left\{ \frac{\phi'(a)}{\phi''(a)} + \frac{1}{3} \frac{\phi'''(a)}{\{\phi''(a)\}^2} \right\} \pm \dots$$

We shall represent the above by  $\pm x^{\frac{1}{2}} \Sigma_\phi$  or simply by  $\Sigma$ . In order that the pair may be real we must have  $x$  and  $\phi''(a)$  of the same sign.

10. As an illustration of the application of the series  $\Sigma$  let us consider the case (a) of  $E_r$ . (ii) in Art. 7. The series  $\rho$  cannot be applied there by choosing  $a=1$ . We shall see that the series  $\Sigma$  is applicable.

Choose  $a=1$ , then

$$x=6, \quad \phi'(a)=-3, \quad \phi''(a)=28,$$

$$\phi'''(a)=48, \quad \phi^{(4)}(a)=24.$$

Now

$$\left\{ \frac{2x}{\phi''(a)} \right\}^{\frac{1}{2}} = \left( \frac{12}{28} \right)^{\frac{1}{2}} = .65466,$$

$$\frac{\phi'(a)}{\phi''(a)} = \frac{-3}{28} = -.10714,$$

$$\frac{1}{3} \frac{x\phi'''(a)}{\{\phi''(a)\}^2} = \frac{2 \times 48}{28 \times 28} = .12245.$$

Hence

$$\begin{aligned} a_2 &= 1 \pm .65466 + .10714 - .12245, \\ &= .98469 \pm .65466, \\ &= 1.63935 \text{ or } .33003, \end{aligned}$$

Calculating also  $a_2\xi^2$  we find  $a_2\xi^2 = \mp .004116$ .

Therefore  $a_2 = 1.63935 - .004116$ ,

or  $a_2 = .33003 + .004116$ .

Thus the pair of roots correct to the second decimal figure is 1.63, .33. If greater accuracy be desired instead of proceeding further along the series  $\Sigma$  it is advisable to choose for  $a$  each of the values 1.63, .33 separately and to apply the series  $\rho$ .

#### *Case when the roots are close together*

11. In the application of the series  $\Sigma$  to find a pair of nearly equal (real) roots it is necessary to choose  $a$  such that  $|\phi'(a)|$  is small and  $x$  and  $\phi''(a)$  have the same sign. When the roots of the pair are close together the choice of  $a$  is difficult to be guessed, but we are guided to the required one by means of the root of  $\phi'(x)=0$

which lies between the pair. The principle will be illustrated in the following example.

Ex. (iii). Solve  $z^4 + 8z^3 - 70z^2 - 144z + 936 = 0$ .

Let us consider the pair of roots lying between 4 and 5.

Take  $\phi(z) = z^4 + 8z^3 - 70z^2 - 144z$ ;

then  $\phi'(z) = 4z^3 + 24z^2 - 140z - 144$ ,

$\phi''(z) = 12z^2 + 48z - 140$ ,

$\phi'''(z) = 24z + 48$ ,

$\phi^{(4)}(z) = 24$ .

Choose  $a=4$ , then  $\phi(a) = -928$ ,  $\phi'(a) = -64$ ,

$\phi''(a) = 244$ ,  $\phi'''(a) = 144$ ,  $\phi^{(4)}(a) = 24$ ;

also  $x = -936 - \phi(a) = -936 + 928 = -8$ .

The signs of  $x$  and  $\phi''(a)$  are not the same.

We proceed to find the root of  $\phi'(z) = 0$  lying between the pair. Applying the series  $\rho$ , the root is given by

$$4 + \frac{64}{244} - \frac{64^2 \cdot 144}{2 \cdot 244^2} + \frac{64^3 \cdot 3 \cdot 144^2 - 244 \cdot 24}{3 \cdot 244^3} -$$

After simplification we obtain the root as 4.244 correct to three places of decimal.

The value of  $|\phi'(a)|$  evidently goes on diminishing as we choose now for  $a$  the following values in succession, viz., 4, 4.2, 4.24, 4.244, ... Of these the value of  $a$  sought must be such that  $x$  and  $\phi''(a)$  have the same sign. Since  $\phi''(a)$  is positive throughout the interval, we are to find now for which of the above values of  $a$ ,  $x$  has a positive sign.

By substitution it is found that for the value 4.24 of  $a$ ,  $x$  is  $-.002$ , so that we must proceed further. We choose then the next value 4.244 for  $a$ . The value of  $x$  being .041 we can now apply the series  $\Sigma$  to get the pair of roots. The labour in computing the values of  $\phi(a)$ ,  $\phi'(a)$  when  $a=4.244$  cannot be avoided but much of it may be curtailed depending on the degree of approximation required.

When an equation has more than two nearly equal roots in a known interval it is easy to conceive that by varying the mode of collecting the terms in  $u_A$  we may find a series applicable in a given case.

12. *Analogous series.* The series  $\rho$  and  $\Sigma$  have been obtained from a consideration of *simple collections* alone. But the mode of collecting terms is not necessarily restricted to simple partial collections only. When we consider suitable *multiple collections* also we may, if we please, obtain other series *analogous* to  $\rho$  or  $\Sigma$ .

13. Up to the present we have discussed rational and integral equations only but in what follows we shall have occasion to pass on to transcendental equations. It is easy to perceive that the methods we have developed may be applied to transcendental equations as well.

*Equivalent series.* The equation  $\phi(z) = \phi(a) + x$  may be put in a form  $\phi(z) = \phi(a) \cdot k$  where  $k$  stands for the quantity  $1 + \frac{x}{\phi(a)}$ . By taking logarithms of both sides the equation  $\phi(z) = \phi(a) \cdot k$  is expressible in the standard form  $\log \phi(z) = \log \phi(a) + \log k$ , when  $\phi(z) = \phi(a) + x$  and  $\log \phi(z) = \log \phi(a) + \log k$  are said to be *equivalent equations*. Evidently a succession of *equivalent equations* may be formed. To each of these equivalent equations the series  $\rho$  or  $\Sigma$  (as the case may be) being applicable a succession of *equivalent series* may be obtained.

### *Transformation of Equations*

14. In applying the series  $\rho$  or  $\Sigma$  to a particular equation some preliminary transformation may appear advantageous. There are only two kinds of transformations, which may be called *rooted* and *non-rooted*. Those transformations which retain the roots in the transformed equation same as those in the original are said to be *rooted*; otherwise the transformations are *non-rooted*. In *non-rooted* transformations we are given the relations which connect the roots of the transformed equation with those of the original.

15. To understand the nature of the advantage gained by a transformation we take the equation in *E.r.* (ii, b), Art 7. When  $a=2$ , the series  $-\phi_{\rho\phi}$  does not yield the root as it is not sufficiently convergent. Let us consider now the following transformation:

Divide the equation  $z^4 + 4z^3 - 4z^2 - 11z + 4 = 0$  throughout by  $z^2$ . This transformation is a rooted one and the resulting equation is

$$z^2 + 4z - 4 - 11z^{-1} + 4z^{-2} = 0.$$

Here

$$\phi(z) = z^2 + 4z - 4 - 11z^{-1} + 4z^{-2},$$

$$\phi'(z) = 2z + 4 + 11z^{-2} - 8z^{-3},$$

$$\phi''(z) = 2 - 22z^{-3} + 24z^{-4},$$

$$\phi'''(z) = 66z^{-4} - 96z^{-5},$$

$$\phi^{(4)}(z) = -264z^{-5} + 480z^{-6};$$

and so on.

When

$$a=2,$$

$$\phi(a) = 3.5,$$

$$\phi'(a) = 9.75,$$

$$\phi''(a) = .75,$$

$$\phi'''(a) = 1.125,$$

$$\phi^{(4)}(a) = -.75.$$

Substituting the above values in the series  $-\phi_{\rho\phi}$  we have

$$\begin{aligned} \alpha_2 &= 2 - \frac{3.5}{9.75} - \frac{(3.5)^2}{|2|} \cdot \frac{.75}{(9.75)^2} - \frac{(3.5)^3}{|3|} \cdot \frac{3(.75)^2 - 9.75 \times 1.125}{(9.75)^3} \\ &= 2 - .358974 - .0049562 + .0007527 \\ &= 1.6368; \end{aligned}$$

which gives the root correct to the third decimal figure.

It is to be noticed that by transformation the new  $\phi'(a)$  happens to be large in comparison to  $\phi''(a)$ .

### McClintock's Method

16. Having shown the advantage gained by a transformation we proceed to consider a standard form of an equation which forms the basis of a method by transformation due to E. McClintock.\* Given an equation  $\phi(z)=0$  (rational and integral) it is possible by means of suitable transformations to express it in McClintock's form  $z^n = \omega^n + naf(z)$  where  $\omega$  is usually an  $n^{\text{th}}$  root of unity. The series obtained by McClintock for a root of the above equation is deducible from  $\rho$ .

\* *American Journal of Mathematics*, Vol. XVII, pp. 89-110.

Let us divide the equation  $z^n = \omega^n + naf(z)$  throughout by  $f(z)$ ; then  $\frac{z^n - \omega^n}{f(z)} - na = 0$  is a rooted transformed equation. Putting  $\psi(z)$  for  $\frac{z^n - \omega^n}{f(z)} - na$ , McClintock's equation is represented by  $\psi(z) = 0$ . Now applying the series  $\rho$  we get the one which is identified as the following due to McClintock.

$$\omega + \omega^{1-n} f(\omega) a + \omega^{1-n} \frac{d}{d\omega} \{f(\omega)\}^2 \frac{a^2}{2} + \left( \omega^{1-n} \frac{d}{d\omega} \right)^2 \omega^{1-n} \{f(\omega)\}^3 \frac{a^3}{3} + \dots \quad (M)$$

By means of the above series McClintock explained a method of calculating simultaneously all the roots of an equation. In the course of development he introduced the ideas of 'dominants' and 'spans' in an equation. The recognition of dominants in a given equation is at the root of his method as the series (M) can then be made convergent by certain definite steps. But his attempts seem to have failed in the case of an equation having nearly equal roots. He puts it as follows:—

"That difficulties will arise when we attempt to apply the formula (M) to cases in which there are no obvious dominants is certain. The case of equal roots has already been mentioned as of that nature."

Ascribing this difficulty to the restricted form of the standard equation used by McClintock we propose to consider the following more general form .

$$\phi(z) = \phi(a) + xf(z).$$

The equation may be put as

$$\frac{\phi(z) - \phi(a)}{f(z)} = x.$$

Representing

$$\frac{\phi(z) - \phi(a)}{f(z)}$$

by  $\psi(z)$  we have the equation expressed in the form  $\psi(z) = \psi(a) + x$ , where  $\psi(a) = 0$

Now 
$$\psi'(a) = \frac{\phi'(a)}{f(a)},$$

$$\psi''(a) = \frac{\phi''(a)}{f(a)} - \frac{2\phi'(a)f'(a)}{\{f(a)\}^2},$$

$$\psi'''(a) = \frac{\phi'''(a)}{f(a)} - \frac{3\phi''(a)f'(a)}{\{f(a)\}^2},$$

$$-3\phi'(a) \frac{f(a)f''(a) - 2\{f'(a)\}^2}{\{f(a)\}^3};$$

and so on.

Substituting the above values in the series  $\rho_\psi$  we can express it in the following convenient form

$$\begin{aligned} a + x \frac{f'(a)}{\phi'(a)} + \frac{x^2}{2} \left( \frac{1}{\phi'(a)} \frac{d}{da} \right) \frac{\{f(a)\}^2}{\phi'(a)} \\ + \frac{x^3}{6} \left( \frac{1}{\phi'(a)} \frac{d}{da} \right)^2 \frac{\{f(a)\}^3}{\phi'(a)} + \dots \end{aligned}$$

when  $\psi'(a)$ , i.e.,  $\phi'(a)$  is small or zero we should apply the series  $\Sigma$  to obtain a pair of nearly equal roots. It must be noticed that McClintock's standard form excludes such a case altogether.

We have not yet considered imaginary roots of an equation. This problem will, however, be taken up in connection with the solution of simultaneous numerical equations which will form the subject of a separate paper in future.

## WEIERSTRASS \*

BY

GANESH PRASAD

1. Karl Theodor Wilhelm Weierstrass was born on the 31st of October, 1815, at Osterfelde in the Münster district of Westphalia. After studying law at the University of Bonn from 1834 to 1838, he went to Münster where he privately studied Mathematics under Gudermann from 1838 to 1840. He was teacher at the Progymnasium of Deutsch-Krone from 1842 to 1848 and head-teacher at the Gymnasium of Braunsberg in East Prussia from 1848 to 1856. He became Honorary Doctor of Philosophy of the University of Königsberg in 1854. In 1856 his research papers on Abelian functions obtained for him an invitation to Berlin as Professor of Pure Mathematics at the Gewerbinstitute and as Member of the Royal Academy of Sciences. In 1856 he also became an extraordinary Professor of the Berlin University and remained there in that capacity until 1864 when he became the third ordinary Professor of Mathematics, the other two being Kummer and Ohm. He remained at the Berlin University until his death which took place after a long illness on the 19th of February, 1897.

2. It is difficult to describe adequately the vast influence which Weierstrass exercised as a lecturer and as a guide of researchers during the forty years of his stay at the Berlin University. Some idea of that influence may be formed by the fact that in the long list of his distinguished pupils are found the names of H. A. Schwarz, Fuchs, Paul du Bois-Reymond, G. Mittag-Leffler, Georg Cantor, Ulissi Dini, Sophie Kowalevsky and Killing. In the circle of his mathematical friends he was looked upon as almost superhuman. According to Professor Mittag-Leffler (*Acta Mathematica*, Vol. 21), it was said: "Weierstrass has indeed something super-human in him. One cannot communicate to him anything which is new to

\* Address delivered before the Allahabad University Mathematical Association on the 3rd December, 1924 as a Patron of that Association.



him ; he knows everything." When Professor Mittag-Leffler went to Paris in 1873 to attend the lectures of Hermite, the first words which the great Frenchman addressed to him gave him a shock. "You have made a mistake," said Hermite "you ought to attend the lectures of Weierstrass at Berlin. He is the teacher of all of us." These were sincere words although uttered by such a patriot as Hermite.

3. As regards the *nature* of the work of Weierstrass as a researcher, there can be no doubt that his work brought to a settlement important issues in the theory of functions of real variables and the theory of functions of a complex variable, and placed the theory of elliptic functions and the theory of Abelian functions on simpler bases. Although the main strength of Weierstrass lay in his logical and critical power, in his ability to give strict definitions and to derive rigid deductions therefrom, he was also skilful in the formal treatment of a given question and in deriving for it an algorithm. Using the language of Professor Felix Klein, according to whom, "among mathematicians in general, three main categories may be distinguished," *viz.*, "logicians, formalists and intuitionists," we shall not be wrong in saying that Weierstrass was emphatically a logician and not an intuitionist.

4. That Weierstrass started in his career as a mathematical investigator with a singleness of purpose, is clear from the following remarks made by him when replying to the Presiding Secretary's words of welcome to him on his entering the Academy of Sciences of Berlin as a member. "I ought now to explain in some words what has been up to this time the course of my studies and in what direction I shall direct myself to pursue them. Since the time when under the direction of my highly revered teacher Gudermann, whom I shall always remember with gratitude, I made acquaintance for the first time with the theory of elliptic functions, this comparatively new branch of mathematical analysis has exercised on me a powerful attraction of which the influence on the entire course of my mathematical development has been decisive. This discipline, founded by Euler, cultivated with zeal and success by Legendre but developed in too one-sided a manner, had at that time since a decade undergone a complete transformation because of the introduction of doubly periodic functions by Abel and Jacobi. Those transcendentals, giving to Analysis new quantities of which the properties are remarkable,

find also manifold applications in Geometry and in Mechanics and show thereby that they are the normal fruit of a natural development of Science. But Abel, habituated to place himself always at the most elevated point of view, had found a theorem which, comprehending all the transcendentals resulting from the integration of algebraic differentials, had the same importance for them as Euler's theorem had for the elliptic functions. Cut off in the flower of his age, Abel could not himself pursue his grand discovery, but Jacobi made a second discovery not less important: he demonstrated the existence of periodic functions of several variables of which the principal properties were founded on the theorem of Abel and by which he made known the true significance of that theorem. The actual representation of those quantities of an entirely new kind of which Analysis had not until then an example and the detailed study of their properties became from that time one of the fundamental problems of Mathematics; and as soon as I comprehended the significance and importance of that problem I decided to attempt its solution. It would have been truly foolish if I had thought of solving that problem without having prepared myself by a profound study of the existent means which could aid me and without exercising them on less difficult problems."

5. For the success of his attack on the Abelian functions, Weierstrass planned roughly as follows (see Poincaré's paper in *Acta Mathematica*, Vol. 22).

I. To build up the general theory of functions, first that of the functions of one variable and then that of the functions of two variables.

II. The Abelian functions being a natural extension of the elliptic functions, to perfect the theory of these latter transcendentals and to show them in a form in which the generalization becomes clear.

III. To attack lastly the Abelian functions themselves.

6. Although the very first of the total number of sixty papers, published by Weierstrass, was a paper on elliptic functions written in the summer of 1840 and partly published in Vol. 52 of *Crelle's Journal* with the title "On the development of modular functions," there is no doubt that Weierstrass kept the aforementioned plan in view and devoted the succeeding six or seven years to a careful investigation of many important points relating to the theory of functions as is evidenced by the next five of his papers. In the seventh paper, published in the annual report of the Gymnasium

of Braunsberg for the year 1848-1849, he attacked the theory of Abelian Integrals. The next paper, published in 1854 in Vol. 47 of *Crelle's Journal* and entitled "About the theory of Abelian Functions," was followed by a paper on the same subject in 1856 in Vol. 52 of *Crelle's Journal*; these papers brought distinction to Weierstrass and led to his transfer to Berlin. During his stay at the University of Berlin from 1856 onwards he was in the habit of communicating many of his discoveries to his students in his lectures.

7. Weierstrass began to lecture on elliptic functions as early as 1857 but the fundamentally new shape which he gave to the theory of elliptic functions may be said to date from the winter of 1862-1863 when he delivered his first systematic course of lectures on that theory. These lectures he continued for several semesters and the results communicated by him appeared first in the form of H. A. Schwarz's "Formulæ and Theorems for the use of elliptic functions" of which the first edition was begun in 1881 and completed in 1885 and the second edition was completed in 1893. Halphen's famous book of which the last volume appeared in 1891 is based on this book. Weierstrass's theory expounded in his lectures has been given in the 5th Vol. of his "Mathematische Werke" which appeared in 1915.

8. Weierstrass's first lectures on Abelian Functions were delivered in 1863 but it is in the systematic course of lectures which he gave on those functions in the winter semester of 1875-1876 and in the summer semester of 1876 that he developed the subject fully and originally. These lectures first appeared as the fourth volume of Weierstrass's "Mathematische Werke" in 1902.

Weierstrass also published papers on partial differential equations, singularities of algebraic curves, theory of quadratic forms, Projective Geometry, Calculus of Variations and Minimal Surfaces. He was interested in the problem of three bodies and once lectured on synthetic Geometry.

9. Weierstrass's last lectures were delivered in the winter of 1889-1890, and his last paper was communicated to the Royal Academy of Sciences in 1891 and bears the title "New proof of the theorem that every integral rational function of a variable can be represented as a product of linear functions of the same variable."

Soon after this time Weierstrass became seriously ill and never recovered his health.

10. Although Weierstrass's genius was of an order different from that necessary for the production of epoch-making papers on the application of Pure Mathematics to Physics, it will be wrong to think that Weierstrass was not aware of the importance of Applied Mathematics. In his address to the Berlin Academy in 1857, part of which I have already quoted, he emphasized this importance in eloquent language and expressed the hope that more functions would be discovered like Jacobi's theta-function which teaches us into how many perfect squares a given whole number can be broken and how the arc of an ellipse can be measured, and which alone can enable us to express the exact law according to which a pendulum swings.

11. I propose now to attempt a difficult task and that is to place before you, in the short time at my disposal, a few concrete examples of Weierstrass's discoveries; I will speak at length about one of them and simply mention the others:—

(a) By giving an example of a function which, while continuous for every value of the variable, did not possess a differential co-efficient for any value of the variable, Weierstrass brought to a settlement an issue which had long agitated the minds of mathematicians. For years before, and after, Ampere's unsuccessful attempt in 1806 to prove that differentiability necessary followed from continuity, most mathematicians believed that, according to what was called the "lex continuitas," such was the case, as they thought that the class of continuous functions was identical with the class of functions representable by graphs. Although Gauss, Dirichlet and Jacobi did not endorse the aforesaid argument, none of them had the conviction that a function which was everywhere continuous but nowhere differentiable could exist. Riemann thought that

$$\sum_{n=1}^{\infty} \frac{\sin(n^a x)}{n^a}$$

was such a function but could not prove his statement.

Weierstrass's non-differentiable function

$$\sum_{n=1}^{\infty} a^n \cos(b^n \pi x),$$

$a$  being any positive proper fraction,  $b$  an odd integer subject to the condition that

$$ab > 1 + \frac{3\pi}{2},$$

was communicated by Weierstrass first in one of his lectures in 1861 and then long afterwards in 1872 to the Royal Academy of Sciences of Berlin; it was published by Paul Du Bois Reymond in *Crelle's Journal*, Vol. 79 in 1876. In *Annali di Matematica*, Vol. 8, Dini gave in 1877 a general type of non-differentiable function modelled after Weierstrass. Weierstrass's function was criticized by C. Wiener in *Crelle's Journal*, Vol. 90; to Wiener's criticisms Weierstrass made an effective reply and pointed out Wiener's misunderstanding. In recent years two attempts have been made to deprive Weierstrass of some credit. (1) One was made in 1915 by Dr. Grace Chisom Young in her Gamble Prize Essay which was published in the *Quarterly Journal of Mathematics*, Vol. 47. Mrs. Young's contention that Cellier's function,

$$\sum_{n=0}^{\infty} \frac{1}{\alpha^n} \sin(\alpha^n x),$$

$\alpha$  being an even integer, which was alleged by her to have been known to Cellier before 1861, had nowhere either a progressive or regressive differential co-efficient and was therefore more truly a non-differentiable function than Weierstrass's function which, at an infinite number of points in any interval ever so small, possessed those differential co-efficients of opposite signs although infinitely large, was shown by Mr. Badri Nath Prasad to be wrong. Mr. Badri Nath Prasad proved (See *Proceedings of the Benares Mathematical Society*, Vol. 3, for 1921-1922 and *Jahresbericht der deutschen Mathematiker Vereinigung*, Vol. 31, p. 174) that Cellier's function was not even non-differentiable as at an infinite number of points in any interval ever so small the function possessed a differential co-efficient infinite in value. (2) The second attempt was made by Dr. M. Jasek of Pilsen (Czechoslovakia) in September 1922 before the German Association of Mathematicians when he stated that Bernard Bolzano had given before 1830 an example of a continuous but nowhere differentiable function. It is, however, a matter of some difficulty to accept this statement when it is known that Bolzano writing his book "Para-

doxien des Unendlichen" in 1847-1848, says in the footnote to Art. 37 that a continuous function must be differentiable for every value of the variable with the exception of "isolated values."

(b) In his paper, entitled "Definition of analytical functions of a variable by means of algebraic differential equations," which was written in 1842, Weierstrass recognized the possibility of the existence of a function with a natural limit; and the first notice in print of such a limit is to be found in a memoir published by Weierstrass in 1866.

(c) Weierstrass's factor theorem, first published in 1876, together with the closely connected Mittag-Leffler's theorem first given in 1877, helped Weierstrass to construct easily the functions  $\wp(z)$  and  $\sigma(z)$  which enabled him to perfect his theory of elliptic functions.

(d) Weierstrass gave a partial differential equation—

$$\frac{\partial^2 \sigma}{\partial z^2} = 12g_2 \frac{\partial \sigma}{\partial g_2} + \frac{1}{3}g_2^2 \frac{\partial \sigma}{\partial g_2} - \frac{1}{12}g_2 z^2 \sigma$$

for  $\sigma(z)$  and used it to expand that function in powers of  $z$  up to  $z^{35}$ . I have requested Mr. Piare Mohan to expand  $\wp(z)$ ,  $\text{sn}(z)$ ,  $\text{cn}(z)$  and  $\text{dn}(z)$  and obtain the general terms. I hope he will do his best to complete the investigation on which he has already entered with enthusiasm.

(e) Jacobi had given the theorem that a function of  $n$  variables could have at the utmost  $2n$  periods. Weierstrass gave a new proof of this theorem carefully laying down the conditions under which the theorem is valid. He then studied the properties of those functions of  $n$  variables which have  $2n$  periods and showed that the properties are analogous to those of elliptic functions.

(f) In a paper published in the *Berliner Berichte* in 1866, Weierstrass gave the parametric representation—

$$x = R\{(1-s^2)F''(s) + 2s F'(s) - 2F(s)\},$$

$$y = R\{i(1+s^2)F''(s) - 2is F'(s) + 2iF(s)\},$$

$$z = R\{2sF''(s) - 2F'(s)\},$$

for the minimal surface, where  $s$  is a complex variable,  $F(s)$  any analytical function of  $s$  and  $R$  denotes that the real part of the expression within the crooked brackets is to be taken.

(g) Weierstrass criticized Dirichlet's principle in 1860 and laid down with care the conditions of its validity.

(h) In a paper written as early as 1842, Weierstrass gave a proof of the theorem known in the theory of functions of a complex variable after Laurent who gave a proof in 1843.

Before concluding this address I wish to thank this large audience of young mathematicians who have listened to me with great attention and to express my fervent hope that some of them will feel inspired by what I have said about Weierstrass and take him as their model in their future careers as mathematical researchers.

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# PHYSICS





## XII. The Electron Theory of Solids and the Rigidity of Metals.

By

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### 1. Introduction.

Sir J. J. Thomson in papers published in the Phil. Mag. (April and October, 1922) has calculated the bulk modulus of elasticity of a number of metals in the solid state on the basis of the cubical atom model proposed by him, and he finds as the expression for the co-efficient of bulk-modulus ( $k$ ), for the alkali metals

$$k = \frac{3 \cdot 65}{9} e^2 \left( \frac{\Delta}{M} \right)^{\frac{1}{3}}$$

where  $e$  is the electronic charge,  $\Delta$  and  $M$  the density and atomic mass of the element respectively. The ideas on which the calculations are made can generally be put in the following words :—

(a) For a monovalent metal the number of electrons per atom is unity: they are distributed at the corners of a cube constructed with the nucleus at the centre; the charges of the nucleus and the electron being  $E$  and  $e$  respectively,  $E$  is equal to  $e$ , in order that the atom may be electrically neutral. For di- and trivalent atoms the number of such disposable electrons is respectively twice and three times the number of atoms, and further  $E$  being  $=2e$  for divalent and  $=3e$  for trivalent metals, the solid is kept electrically neutral.

(b) The solid is built up of such cubical cells packed together to fill space and the different atoms and electrons composing the solid are kept in equilibrium by the joint

action of their mutual attractions and repulsions according to laws of force, (i) varying according to the inverse square and (ii) varying according to the inverse cube of the distance.

The question of the rigidity of the type of structure postulated by Sir J. J. Thomson arises naturally and does not appear to have been considered so far. In the present paper an expression for the co-efficient of simple rigidity of such atomic structures is obtained for mono-, di-, and tri-valent metals and some of the results so obtained are compared with the experimentally determined values of the co-efficient. It is assumed throughout this paper that the thermal motion of the electrons composing the atoms is *nil*, or in other words, the different atoms and electrons are fixed in their position in space, so that the results obtained take no account of the temperature co-efficient of the constants of rigidity of these elements.

The paper also describes special experiments made to determine the modulus of rigidity of the alkali metals sodium and potassium.

## 2. *Method of evaluating the co-efficient of rigidity.*

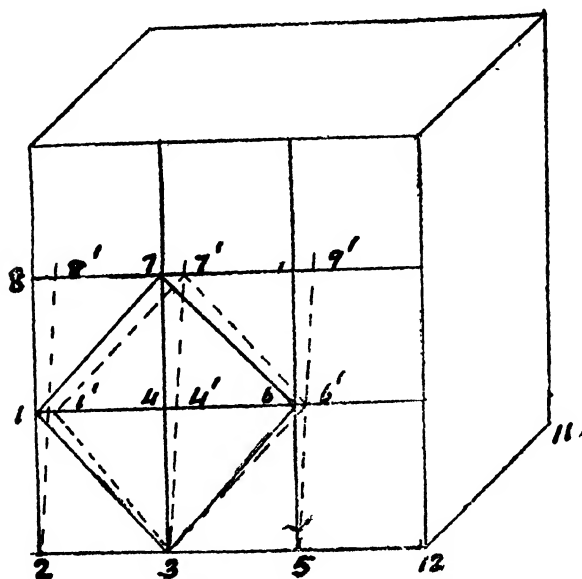


Fig. I.

In the classical theory, there are two ways of regarding a shear (i) where the particles of the body are pushed forward by a tangential force as shown in Fig. 1 (the cube 1234 is strained into 1'234'), (ii) the other way is to consider it as an extension in one direction combined with an equal contraction in a direction at right angles to the extension. In the spacial distribution of electrons constituting the atoms of a solid metal, the electrons or nuclei occupy the corners of cubes. Here the two methods of regarding a shear are identical, for what is shear of the former type for the cube 1234, is shear of the latter type for the cube 1367, combined with a rotation of the sheared system through a finite angle. This rotation as a rigid body will not involve any relative motion of the parts of the system and will not call into play any forces depending upon the elasticity of the system. In both these types of shear the work done is stored up as the increase of potential energy of the sheared structure and is equal to  $\frac{1}{2}T\theta$  or  $\frac{1}{2}n\theta^2$ , where  $T$  is the tangential stress or pull or push per unit area,  $n$  is the co-efficient of rigidity and  $\theta$  the angle of shear. The increase of potential energy of any electron or nucleus such as 2 (Fig. 1) is obviously the contribution of a series of electrical doublets all directed in the direction of strain and situated at the corners of the undeformed cubes, such as shown in Fig. 1 by 11', 44', 66', etc. The displacements below the datum plane are oppositely directed to those above it. Thus the increase of potential energy for the electron 2 is to be obtained on evaluating  $\frac{1}{2}\Sigma e\Omega_{..}$ , where  $\Omega_{..}$  is the potential at 2 of any doublet due to displacement of electron or nucleus at S. Similarly for a nucleus at 2 the increase of potential energy is to be obtained on evaluating  $\frac{1}{2}\Sigma E\Omega_{..}$ . Generally the increase of potential energy per unit volume is to be obtained in the form

$$W = k_1\theta^2 + k_2\theta^4 + k_3\theta^6 + \dots$$

where  $k_1, k_2, k_3$ , etc., are functions of  $e$  and  $d$  (the side of the cube). Since the force is of the two types (i) the inverse

square and (ii) the inverse cube, and act in opposition for equilibrium  $\Omega_s$ , is of the form

$$\Omega_s = f \cdot \frac{2\mu \cos \phi}{r^3} - \frac{\mu \cos \phi}{r^3}$$

where  $f$  as determined from the conditions for equilibrium  $= 1.825d$ ;  $r$  is the distance of the doublet 2 from  $s$ ,  $\mu$  is the moment of the doublet,  $\cos \phi$  is the cosine of the angle of inclination of 2S to the plane of the doublet and is expressible in terms of  $d$  and  $\theta$ .

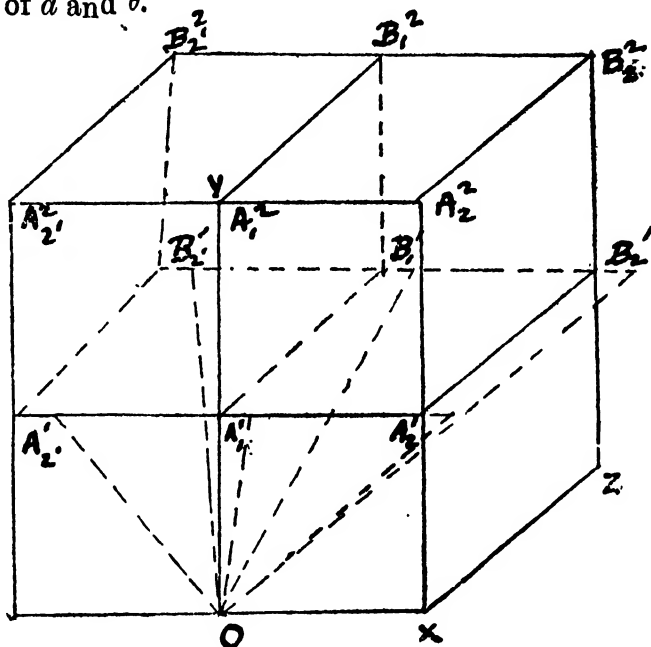


Fig 2.

The method of calculation is to take the joint effect of the doublets on both sides of the YZ plane. As nearly equiposed pairs of doublets  $A'_2$  &  $A'_2$ ,  $A''_2$  &  $A''_2$ ,  $B'_2$  &  $B'_2$ , leave a slight positive or negative balance, the calculation for the total contribution for any point O can be made by adding the effects of such pairs of doublets in the different layers and rows. Planes parallel to XYO being called rows, the plane XY is the first of the rows; planes parallel to XYO being called layers, ZYZ' is the first layer.

<sup>1</sup> Phil. Mag., Vol. 43, p. 735.

The contributions for the different layers and rows are given by the following expressions. The doublets nearest the plane OYB—such as A', B', C', etc., being taken singly and the rest in pairs. Only a few expressions are given here; the rest follow easily:

Inverse square law

$$\begin{aligned} & \left[ \begin{array}{l} \text{1st row} \\ \text{1st layer} \end{array} \right] \begin{array}{l} A'_1 \\ A'_2 \text{ \& } A'_3 \end{array} \begin{array}{l} \frac{ex^2}{(d^2+x^2)^{\frac{3}{2}}} \\ ex \left[ \frac{d+x}{\{d^2+(d+x)^2\}^{\frac{3}{2}}} - \frac{d-x}{\{d^2+(d-x)^2\}^{\frac{3}{2}}} \right] \end{array} \\ & \left[ A'_3 \text{ \& } A'_2, ev \right] \left[ \frac{2d+x}{\{d^2+(2d+x)^2\}^{\frac{3}{2}}} - \frac{2d-x}{\{d^2+(2d-x)^2\}^{\frac{3}{2}}} \right] \end{aligned}$$

Inverse cube law

$$\begin{aligned} & f \cdot \frac{ex^2}{(d^2+x^2)^3} \times 2 \\ & e'f \left[ \frac{d+x}{\{d^2+(d+x)^2\}^3} - \frac{d-x}{\{d^2+(d-x)^2\}^3} \right] \times 2 \\ & e'f \left[ \frac{2d+x}{\{d^2+(2d+x)^2\}^3} - \frac{2d-x}{\{d^2+(2d-x)^2\}^3} \right] \times 2 \\ & f \frac{e'x^2}{(2d^2+x^2)^3} \\ & e'f \left[ \frac{d+x}{\{2d^2+(d+x)^2\}^3} - \frac{d-x}{\{2d^2+(d-x)^2\}^3} \right] \times 2 \end{aligned}$$

$$\begin{aligned} & \left[ \begin{array}{l} \text{2nd row} \\ \text{1st layer} \end{array} \right] \begin{array}{l} B'_1 \\ B'_2 \text{ \& } B'_3, ev \end{array} \begin{array}{l} \frac{ex^2}{(2d^2+x^2)^{\frac{3}{2}}} \\ \left[ \frac{d+x}{\{2d^2+(d+x)^2\}^{\frac{3}{2}}} - \frac{d-x}{\{2d^2+(d-x)^2\}^{\frac{3}{2}}} \right] \end{array} \end{aligned}$$

$$\begin{aligned} & \left[ \begin{array}{l} \text{1st row} \\ \text{2nd layer} \end{array} \right] \begin{array}{l} A''_1 \\ 2ex \left[ \frac{d+2c}{\{4d^2+(d+2c)^2\}^{\frac{3}{2}}} - \frac{d-2c}{\{4d^2+(d-2c)^2\}^{\frac{3}{2}}} \right] \end{array} \\ & f \frac{\frac{1}{2}ex^2}{(4d^2+4c^2)^3} \times 2 \\ & 2e'f \left[ \frac{d+2c}{\{4d^2+(d+2c)^2\}^3} - \frac{d-2c}{\{4d^2+(d-2c)^2\}^3} \right] \times 2 \end{aligned}$$

For the electrons and nuclei situated at the centres of the cubes, similar expressions are obtained by putting  $\frac{x}{2}$  for  $x$  and  $\frac{d}{2}$  for  $d$  in the expressions such as for  $B', B','$ , etc. Thus for the nuclei at the centres of the cubes  $OA', B', B',$  and  $OA', B', B','$  the inverse square law gives

$$-\frac{1}{2}ex \left[ \frac{\frac{d+x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d+x}{2}\right)^2 \right\}^{\frac{3}{2}}} - \frac{\frac{d-x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d-x}{2}\right)^2 \right\}^{\frac{3}{2}}} \right]$$

and the inverse cube law gives

$$-\frac{1}{2}exf \left[ \frac{\frac{d+x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d+x}{2}\right)^2 \right\}^{\frac{5}{2}}} - \frac{\frac{d-x}{2}}{\left\{ 2\left(\frac{d}{2}\right)^2 + \left(\frac{d-x}{2}\right)^2 \right\}^{\frac{5}{2}}} \right] \times 2$$

The sign before the last two expressions is to be reversed if the two cubes contain electrons instead of nuclei. Similar expressions hold good for the other pairs in succession.

Assuming  $\frac{x}{d}$  or  $\theta$  small enough so that powers higher than the square of  $\theta$  can be neglected, the above expressions can be simplified and the results are given in the appendix A. The successive figures in the vertical columns indicate the results of pairs taken in order, two every time on both sides of the  $yz$  plane. All these results are for the doublets in quarter the whole strained structure, so that from the symmetry of the doublets if we take the moment of those in row 1 as  $\frac{1}{4}ec$  instead of  $e$ , the total increase in the potential energy of an electron or nucleus is twice as shewn by the figures with appropriate signs in the tables, the expression being  $\frac{1}{2}\Sigma e\Omega_{2s}$  or  $\frac{1}{2}\Sigma E\Omega_{2,s}$ . In actual summation, as shewn in the

case of the alkali metals below, the contributions are mainly those due to the eight cubes meeting at the point, the rest add a slight correction term and the contributions are therefore taken so as to be correct to the first decimal figure.

### 3. *Alkali Metals.*

For metals of this group, there is one electron for each atom, and further  $E=e$ . Since all of these metals crystallize in the regular system the nuclei being situated at the centres of the small cubes, the electrons are situated at the corners—one for each corner. As each corner is the meeting place of eight cubes, if we consider the effective electron charge for each cube, at any of the corners to be  $e/8$ , there being eight such corners for a cube, the total electronic charge is  $e$  for each cube which contains the nuclear charge  $E$  at its centre. To calculate the increase of potential energy of an electron we find for the eight cubes meeting at 2 (Fig. 1),

for the inverse square law

$$\begin{aligned}\frac{1}{2}\sum e\Omega_{2s} &= 2(+0.500 - 0.177 + 0.354) \frac{\theta^2 e^2}{d} \\ &= 1.354 \frac{\theta^2 e^2}{d}\end{aligned}$$

and for the inverse cube law

$$\begin{aligned}\frac{1}{2}\sum e\Omega_{2s} &= 4(0.500 + 0.250 - 0.250 - 0.074 + 0.296) \frac{\theta^2 e^2}{d^2} f \\ &= 2.888 \frac{\theta^2 e^2}{d^2} f\end{aligned}$$

A few succeeding terms of the series obtained by adding a layer of one cube every time around these eight cubes are

$$+0.173, +0.085, -0.095, -0.047, \times \frac{\theta^2 e^2}{d}$$

according to the inverse square and

$$-0.023, -0.108, -0.088, +0.017, \times \frac{2\theta^2 e^2}{d^2} f$$

according to the inverse cube law of force.



Correcting, therefore, the increase of potential energy per unit volume of  $N$  cubes (each  $e$  and  $E$  being reduced to  $\frac{1}{8}$ th its value for each corner of a cube), as given by

$$\begin{aligned} & \frac{1}{2} N \Sigma e \Omega_{,,} + \frac{1}{2} N \Sigma E \Omega_{,,} \\ &= \frac{1}{64} \left( 4 \cdot 18 f \frac{\theta^3 e^3}{d^3} - 3 \cdot 2 \frac{\theta^3 e^3}{d} \right) N \end{aligned}$$

The work of a shearing stress per unit volume  $= \frac{1}{2} n \theta^2$  where  $n$  is the co-efficient of rigidity.

Thus we have the equations,

$$\left. \begin{aligned} \frac{1}{2} n \theta^2 &= \frac{1}{64} \left( 4 \cdot 18 f \frac{\theta^3 e^3}{d^3} - 3 \cdot 2 \frac{\theta^3 e^3}{d} \right) N. \\ N d^3 &= 1 \text{ and } N M = \Delta \end{aligned} \right\} \quad \dots (1)$$

Substituting the value of  $f$  and  $N$  in (i)

we have,

$$n = \frac{4 \cdot 4 e^3}{32 d^4} = \frac{1 \cdot 1}{8} e^3 \left( \frac{\Delta}{M} \right)^{\frac{4}{3}}$$

The following table shews the calculated values of  $n$  against those observed by the author, as described in the next section.

*Table I*

Metal.			Calculated $n$ dynes per sq. cm.	Observed $n$ dynes per sq. cm.
Lithium	...	...	$0 \cdot 499 \times 10^{11}$	.....
Sodium	...	...	$0 \cdot 218 \times 10^{11}$	$0 \cdot 192 \times 10^{11}$
Potassium	...	...	$0 \cdot 093 \times 10^{11}$	$0 \cdot 068 \times 10^{11}$
Rubidium	...	...	$0 \cdot 075 \times 10^{11}$	.....
Caesium	...	...	$0 \cdot 053 \times 10^{11}$	.....

#### 4. *Experimental confirmation.*

The great difficulty in the determination of the elastic constants of the alkali metals is the vigorous chemical action that takes place when these metals are exposed to the moisture-laden atmosphere; sodium melts away while in the case of potassium the action is attended with fire. Experiments are, therefore, to be made (i) in an inert atmosphere of pure nitrogen or pure hydrogen, or as can be more easily be availed of in an atmosphere of ether-vapour, completely dehydrated by being previously treated with an excess of metallic sodium in a closed vessel, (ii) by dipping the metal in anhydrous kerosine. In both these processes the results are liable to considerable error, by the admission of the slightest amount of the water vapour that may get access to the vessel, owing to formation of a thin crust of hydroxide on the surface of the metal wire. Experiments of a preliminary nature were undertaken avoiding the above difficulties as far as possible, the necessary manipulative skill being acquired by practice.

Sodium being drawn into a wire of 1.4 mm. diameter by pressing the metal through the nozzle of the sodium press, was at once transferred to the previously prepared atmosphere of anhydrous ether-vapour in a tall glass cylinder closed by a lid and the wire was subsequently hung from a torsion head and a cylindrical weight of known moment of inertia was fastened at the lower end of the wire. Gentle torsion could be applied by the head being twisted from outside and the period of the resulting oscillation, which lasted only for about a second, was measured by photographic registration of a spot of light reflected from a mirror attached to the inertia cylinder, along with the records of a tuning fork of frequency 60 per sec. Thus it was found that for a sodium wire of length 78 cms. and radius 0.677 mms. carrying a load of which the calculated moment of inertia was 13.2 units,

the vibration period was 0.25 second. From the approximate formula  $n = \frac{8\pi kl}{t^2 r^2}$  where  $n$ ,  $k$ ,  $l$ ,  $r$ ,  $t$  are the rigidity co-efficient, the moment of inertia of the weight, the length, the radius and the period of vibration of the wire respectively,  $n$  is calculated to be  $1.92 \times 10^{10}$  dynes per sq. cm. which is closely in agreement with the theoretically calculated value.

For potassium, the procedure adopted in the case of sodium could not be followed on account of its greater chemical activity. Accordingly, a heavy cylindrical weight of mass, about 250 grammes, was hung from a fine wire suspension so that the system when twisted had a period of vibration 7 to 8 seconds. A short piece of potassium wire prepared as in the case of sodium was fixed to the lower end of this cylinder. The other end of the wire was fixed to a massive weight resting at the bottom of a glass vessel filled with kerosine; so that the whole of the potassium wire was merged in the oil. On being gently twisted, and released the system was found to vibrate for a short time with a period of about  $\frac{1}{4}$ th of a second, which was measured by the optical method of registration as before. The result found for the co-efficient of rigidity of potassium was  $6.8 \times 10^9$  dynes per sq. cm. as against the calculated value  $9.3 \times 10^9$ . The discrepancy in the results both for sodium and potassium is probably to be attributed to the error in the estimation of the mean radius of the wire.

Experiments with other alkali metals have not yet been attempted.

### 5. *Copper Group.*

Although the elements of this group (copper, silver and gold) exhibit varying valency, they are generally considered to be related to the alkali metals in their monovalent character and the regular system in which they all crystallize. But their case stands out different from the structure of

monovalent elements given by Sir J. J. Thomson. Applying the formula for the bulk modulus ( $k$ ) to these metals the calculated values are much less than the observed values and so are the calculated values of  $n$ . Table 2 shews the calculated and observed values of  $k$  and  $n$  for copper, silver and gold. It will be observed that the calculated values are roughly about one-fourth the observed values. The difficulty as regards these elements is obviated if the atomic structure is assumed to have twice the electronic charge and twice the nuclear charge instead of one as in the case of the alkali metals. On this assumption, the calculated and observed values shew a better agreement (Table 2, columns 3-4, and 6-7).

Table II.

1	2	3	4	5	6	7
Element.	$k$ Calculated from Thom- son's formula for the alkali metals.	$k$ Calculated on the assumption $E = e = 2e$ .	$k$ Observed.	$n$ Calculated from the formula for the alkali metal.	$n$ Calculated on the assumption $E = 2e = e$ .	$n$ Observed.
Copper...	$3.68 \times 10^{11}$	$14.74 \times 10^{11}$	$14.3 \times 10^{11}$	$1.13 \times 10^{11}$	$4.52 \times 10^{11}$	$4.55 \times 10^{11}$
Silver ...	$2.30 \times 10^{11}$	$9.21 \times 10^{11}$	$10.9 \times 10^{11}$	$0.72 \times 10^{11}$	$2.88 \times 10^{11}$	$2.87 \times 10^{11}$
Gold ...	$2.41 \times 10^{11}$	$9.64 \times 10^{11}$	$16.5 \times 10^{11}$ $12.5 \times 10^{11}$	$0.73 \times 10^{11}$	$2.92 \times 10^{11}$	$2.77 \times 10^{11}$

<sup>1</sup> The latter value is that found by Buchanan (Proc. Roy. Soc., 1904).

## 6. Di-valent and Tri-valent metals.

### *Aluminium.*

A trivalent element when in a solid state must have three electrons for each atom. And if it crystallises in the regular system each atom is to be surrounded by a rhombic dodecahedra of electrons which, when packed together to fill space, are

equivalent to any one of the following space lattice arrangements :

1. Cubical cells—with the nuclei at the corners of the cell and also at the centre of its faces. The electrons are situated at the middle points of the edges of the cell, at the centres of the 8 cubes into which the cell is divided by planes bisecting its edges at right angles. One electron is placed at the centre of the cell. This arrangement gives 4 atoms and 12 electrons per cell.

2. Cubical cells—with nuclei at the middle points of the edges of the cell and one is at the centre of the cell. The electrons are placed at the corners and the centres of the faces and at the centres of the 8 cubes into which the cell is divided by planes bisecting its edges at right angles. This arrangement also gives 4 atoms and 12 electrons per cell.

3. Cubical cells—in which the nuclei are situated at the centres of 4 small cubes, forming the corners of a regular tetrahedron. The electrons are placed at the corners of the large cell, the centres of its edges and at the centres of the small cubes not occupied by the nuclei and one is at the centre of the cell. This arrangement also gives 4 atoms and 12 electrons per cell, of eight small cubes.

In order to calculate the co-efficient of rigidity the increase of potential energy per atom is calculated according to the method used in sections 2 and 3, by putting  $E=3e$ .

Using arrangement (1) the increase of potential energy per electron due to doublets of shear in the eight small cubes is found to be  $+6.29 \frac{\theta^2 e^2}{d^2} f$  due to the inverse cube law of force and  $+1.65 \frac{\theta^2 e^2}{d^2}$  according to the inverse square law.

<sup>1</sup> A cell is used to denote a cube with side  $2d$  and is composed of 8 small cubes.

Using arrangement (2) the corresponding increases of potential energy of a nucleus are  $+1.6\frac{\theta^2 e^2}{d^2}f$  and  $-0.186\frac{\theta^2 e^2}{d^2}$  respectively.

Using arrangement (3) the respective increases are  $-1.7\frac{\theta^2 e^2}{d^2}f$  and  $-3.56\frac{\theta^2 e^2}{d^2}$ .

Since each atom of aluminium is made up of one electron of type (1) one nucleus of type (2) and two electrons of type (3) the total increase is

$$12.79\frac{\theta^2 e^2}{d^2}$$

Thus, as in Section 3

$$n_{Al} = \frac{12.79}{32} \frac{e^2}{d^2} N$$

Now  $NM = \Delta$  as before and since 4 atoms are contained in a volume  $(2d)^3$

$$\frac{1}{d} = 2^{\frac{1}{3}} \left( \frac{\Delta}{M} \right)^{\frac{1}{3}}$$

Thus

$$n_{Al} = \frac{12.79}{32} e^2 2^{\frac{1}{3}} \left( \frac{\Delta}{M} \right)^{\frac{1}{3}}$$

$$= 2.72 \times 10^{11} \text{ dynes per sq. cm.}$$

$$\Delta_{Al} = 2.70 \qquad M_{Al} = 27.1 \times 1.64 \times 10^{-24} \text{ grms.}$$

The value of it found from the tables is  $2.67 \times 10^{11}$ , which agrees fairly well with the calculated value.

*Calcium.*

Of the divalent metals calcium is the one that crystallises in the regular system: the other divalent metals Mn, Zn, Cd, crystallize in the hexagonal system in which the elastic properties vary in different directions. The compressibility of calcium has been calculated by Sir J. J. Thomson using Hull's structure of its crystals and is found to be  $5.9 \times 10^{-12}$  against the experimental value  $5.5 \times 10^{-12}$ .

The crystal of the metal is built up according to the following scheme. Cubical cells—having  $\frac{1}{8}$ th of a nucleus at each corner and  $\frac{1}{2}$  of an atom at the centre of each of its six faces. This makes the total number of nuclei four. The electrons are arranged at the middle point of each side of the cell, one electron at the centre of the cell and one electron each at the centres of the four out of the eight small cubes into which the larger cell is divided by planes bisecting its edges at right angles. These four cubes are chosen so that if one moves parallel to any side of the cell the empty cubes and those containing electrons occur alternately.

Neutral calcium atom consists of one positive nucleus and two electrons—one of the type in which it occurs at the middle point of a side of the cell and the other in which it occurs at the centre of a small cube and for its divalency  $E=2e$ .

The contributions to the increase in the potential energy of the nucleus and the two types of electrons are found to be respectively

$$+2.81 \frac{\theta^2 e^2}{d^3} f, 3.99 \frac{\theta^2 e^2}{d^3} f$$

and 0, for the inverse cube law of force;

$$+0.58 \frac{\theta^2 e^2}{d}, +2.35 \frac{\theta^2 e^2}{d}$$

and 0 for the inverse square law of force.

Thus for the total increase, putting

$$f=1.825d,$$

we get

$$9.47 \frac{\theta^2 e^2}{\bar{d}}$$

For this metal

$$\frac{1}{\bar{d}} = \left( \frac{2\Delta}{M} \right)^{\frac{1}{3}}$$

Thus  $n$  for calcium

$$= \frac{9.47}{32} e^2 2^{\frac{1}{3}} \left( \frac{\Delta}{M} \right)^{\frac{1}{3}}$$

Where

$$\Delta = 1.85$$

$$M = 40 \times 1.64 \times 10^{-24} \text{ grms.}$$

The calculated value of  $n$  is  $7.47 \times 10^{10}$ . The experimental value for  $n$  is not available.

## 7. *Summary and Conclusion.*

Calculations of the co-efficient of rigidity of the alkali metals have been made on the basis of the atom model proposed by Sir J. J. Thomson (Phil. Mag., Vols. 43 and 44), and the results obtained have been experimentally verified for sodium and potassium. The calculations include the cases of the apparently complex structures of the metals, copper, silver and gold, which are generally considered to be related to the alkali metals in their monovalent character and the regular system in which they all crystallize. The calculations are extended to the case of the trivalent aluminium and divalent calcium and good agreement is found between the calculated and the observed values for aluminium.



In conclusion, the present writer wishes to accord his best thanks to Prof. C. V. Raman for drawing the writer's attention to the problem and for many valuable criticisms and corrections during the progress of the work.

CALCUTTA,

*The 3rd September 1923.*

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APPENDIX A.  
INVERSE CUBE LAW.  
*Electrons.*

1st row.			2nd row.			3rd row.		
1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.
$\times 2 \frac{\theta^2 e^3}{d^3} f$	$\times 2 \frac{\theta^2 e^3}{d^3} f$	$\times 3 \frac{\theta^2 e^3}{d^3} f$	$\times \frac{\theta^2 e^3}{d^3} f$	$\times 2 \frac{\theta^2 e^3}{d^3} f$	$\times 3 \frac{\theta^2 e^3}{d^3} f$	$\times \frac{\theta^2 e^3}{d^3} f$	$\times 2 \frac{\theta^2 e^3}{d^3} f$	$\times 3 \frac{\theta^2 e^3}{d^3} f$
+0.500 -0.250 -0.087 -0.026 -0.009	+0.062 +0.016 -0.002 -0.002 -0.010	+0.018 +0.018 -0.003 -0.009 -0.0012	+0.250 -0.074 -0.092 -0.037 -0.015	+0.080 +0.036 -0.038 -0.032 -0.016	+0.030 +0.030 -0.003 -0.015 -0.012	+0.040 +0.018 -0.019 -0.016 -0.009	+0.030 +0.026 -0.008 -0.014 -0.010	+0.018 +0.021 0.000 -0.006 ...

*Nuclei.*

1st row.			2nd row.			3rd row.		
1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.
$\times \frac{1}{2} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{2}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{5}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{1}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{2}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{5}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{1}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{2}{3} \frac{\theta^2 e^3}{d^3} f$	$\times \frac{5}{3} \frac{\theta^2 e^3}{d^3} f$
-0.592 -0.300 -0.059 -0.017	+0.252 -0.118 -0.072 -0.031	+0.093 -0.001 -0.029 -0.022	+0.084 +0.039 -0.024 -0.010	+0.104 +0.021 -0.017 -0.020	+0.057 +0.007 -0.015 -0.015	+0.019 +0.000 -0.006 -0.004	+0.034 +0.004 -0.009 -0.009	+0.030 +0.008 -0.004 -0.007

APPENDIX A.  
INVERSE SQUARE LAW.  
*Electrons.*

1st row. <sup>1</sup>			2nd row.			3rd row.		
1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.
$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$
+1.000 -0.854 -0.250 -0.107 -0.052	+0.250 +0.143 -0.088 -0.092 -0.062	+0.111 +0.132 -0.009 -0.039 -0.044	+0.354 +0.000 +0.000 -0.079 -0.044	+0.178 +0.136 -0.049 -0.071 -0.089	+0.095 +0.119 +0.016 -0.030 -0.038	+0.089 +0.068 -0.024 -0.035 -0.026	+0.088 +0.049 +0.000 -0.033 -0.034	+0.064 +0.090 +0.025 -0.013 -0.025

*Nuclei.*

1st row. <sup>1</sup>			2nd row.			3rd row.		
1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.	1st layer.	2nd layer.	3rd layer.
$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$	$\times \frac{\theta^2 e^2}{d}$	$\times 2 \frac{\theta^2 e^2}{d}$	$\times 3 \frac{\theta^2 e^2}{d}$
+0.000 -0.317 -0.100 -0.040 -0.020	+0.477 -0.121 -0.132 -0.078 -0.048	+0.252 +0.044 -0.050 -0.058 -0.080	+0.160 -0.040 -0.044 -0.024 -0.015	+0.243 +0.000 -0.062 -0.051 -0.036	+0.173 +0.050 -0.023 -0.033 -0.045	+0.048 +0.008 -0.004 -0.011 -0.009	+0.104 +0.031 -0.014 -0.020 -0.027	+0.076 +0.046 +0.000 -0.048 -0.022

<sup>1</sup> These figures are to be taken halved in calculation.

## XIV. On the Colours of Colloids in relation to the size of the dispersed particles.

By

BIDHUBHUSAN RAY, D.Sc.,

*Lecturer in Physics, Calcutta University.*

The colour and polarisation of light scattered in all directions by particles not very small in comparison with the wave-lengths of light have been studied experimentally by Steubing,<sup>1</sup> Schirman,<sup>2</sup> Paris,<sup>3</sup> Ray,<sup>4</sup> and others and on the whole their results agree with the mathematical explanation of the action of turbid media on light given by Rayleigh<sup>5</sup> and Mie<sup>6</sup> from the point of view of the electromagnetic theory. But the colours of the transmitted light which have an important practical application in the colours of metal glasses, and also the changes of colours of colloidal solutions during coagulation and the axial colours exhibited by clouds of liquid droplets suspended in air as observed by Barus,<sup>7</sup> have so long been imperfectly understood, and no attempt has been made to bring these phenomena under general theoretical consideration. An attempt will be made in the present paper in the last-named direction.

In order to explain the experimental results of Keen<sup>8</sup> and Porter, on the transmitted colour of sulphur suspensions, Rayleigh<sup>9</sup> attempted the solution from energy considerations.

<sup>1</sup> Ann. der. Phys. 26, 1908.

<sup>2</sup> Ann. der. Phys. 59, 1919.

<sup>3</sup> Phil. Mag. Vol. 30, 1915.

<sup>4</sup> Proc. Ind. Ass. Vols. 7 and 8.

<sup>5</sup> Scientific Papers Vols. I and 4.

<sup>6</sup> Ann. der. Phys. 25, 1908: Koll. Zeit., 1907.

<sup>7</sup> Smithsonian contributions 1901, 1903.

<sup>8</sup> Proc. Roy. Soc. Vol. 89, Ser. A, 1914.

<sup>9</sup> Proc. Roy. Soc. Vol. 90, Ser. A, 1914.

The energy of the scattered light which increases rapidly as the size of the particles increases, is derived from the primary beam and hence the energy of the transmitted light decreases *pari passu*, as it passes through the medium with the increase in the proportion of the energy scattered. This only leads to the result that as the particles grow in size, the suspension refuses to transmit first the shorter waves and then finally the whole visible spectrum. Lord Rayleigh did not however find it possible to explain the reappearance of the transmitted light in the later stages, observed by Keen and Porter (*l. c.*).

Garnett<sup>1</sup> has exhaustively dealt with the colours of metal glasses and of the colloidal solutions of gold and silver. Following Rayleigh, Larmor and others, he first showed that a metal sphere, small compared with the wave-length of light, produces in all surrounding space the same effect as would be produced by a Hertzian doublet placed at its centre. He further showed that, considering a volume which in all its directions is great compared with the wave-length of light and provided the particles are many to a wave-length of light, the suspensoid with its dispersed particles is optically equivalent to a complex medium, whose refractive index and extinction co-efficient depend on those of the particles and of the medium. The colours of the metal glasses and of the metal sols are now explained by Garnett as light absorption by the new complex medium, but the experimental results agree with the theoretical deductions only when the particles are very small, *e.g.*, the transmitted colour is red or yellow. It seems that the transmitted blue-violet colours, *i.e.*, when the particles are larger than in the previous case, cannot be explained on the lines followed by Garnett who suggests in these cases that the particles selectively reflect red and yellow rays and hence the fluid appears blue-violet. But it is extremely doubtful that such a reflection really occurs even when the size

<sup>1</sup> Phil. Trans., Ser. A, Vols. 203 and 205.

of the particles is about  $100\mu\mu$ . The limitation of this treatment can be seen if the fundamental assumptions are examined more closely. As the particles grow larger, they are not many to a wave-length of light, so that the idea of the complex medium breaks down and we have to examine the light scattering by discrete particles embedded in the medium and distributed in any specified manner.

## 2. *The Theory of the Colours.*

The energy scattered by the particles is derived from the primary beam and hence the intensity of the latter must suffer an attenuation as it passes through the medium. The co-efficient of attenuation is usually derived by a simple calculation of the total energy scattered by an individual particle and then multiplying this by the number of particles per unit volume and then deducting the result from the intensity of the transmitted light. This method is however open to criticism, as it ignores the effects due to the interference of the primary and scattered waves. The more accurate method for the determination of the attenuation co-efficient would be to compound the primary wave with the secondary waves scattered by the particles in the primary direction, with their proper amplitudes and phases. On these considerations, Raman and Ray<sup>1</sup> successfully explained the colours of sulphur suspensions observed by Keen and Porter. It will be seen that the method proposed by Raman and Ray is a general one and applicable to the colours of metal glasses, of hydrosols, and of aero-sols, and other allied phenomena.

The colours of colloids depend on the nature of the particles and of the media, on the shape and size of the particles, and also on their number per unit volume. We shall, for simplicity, assume the shape of the particles to be spherical (as assumed by Garnett, Rayleigh and others) and also that the

<sup>1</sup> Proc. Roy. Soc. Ser. A, Vol. 100.

particles are distributed at random. Consider the passage of a plane wave front through a thin layer of the medium containing  $n$  scattering particles per unit volume. We may, following Rayleigh, divide the wave front into elementary areas in accordance with the Fresnel-Huyghens principle, the effect of the secondary waves diverging from these elements at an external point being integrated to find the amplitude and phase of the transmitted wave. In the present case an appreciable part of the area of the wave front is occupied by the scattering particles, which are supposed to be sufficiently numerous and irregularly arranged. We have to consider this part separately from the rest of the wave front. The attenuation of the light in passing through the medium is, according to this procedure, seen to be due to two causes :—

(1) the decrease in the area, and consequently also of the resultant effect of the undisturbed portion of the wave-front ; and

(2) the interference with this of the light scattered in the direction of the primary wave by the particles lying in the wave front.

In the case of the very finest particles, the effect contemplated in (1) is very small and the phase of the scattered waves in relation to that of the primary waves is such that the interference effect referred to in (2) does not (to a first approximation) alter the amplitude of the resulting effect, but only affects its phase. With increasing size of the particles, however, the case is altered. The effect (1) becomes considerable and results in a continuous decrease in the transparency of the medium with increasing size of the particles, the number being assumed to be the same. The amplitude of the light scattered by individual particles also increases rapidly at the same time, and the importance of the effect (2) is therefore enhanced ; but whether this results

in an increase or decrease of the amplitude of the transmitted wave obviously depends on the phase relationship between the primary and scattered waves in the direction of regular propagation. If the phase of the scattered waves lags sufficiently behind that of the primary waves, we may have actually an increase in the resulting transmission of the light by the suspension with increase in the size of the particles. As we shall see presently, this is what actually happens. Following Raman and Ray (*l. c.*) we are now in a position to write down the expression for the co-efficient of transmission of light through the suspension. Assuming the amplitude of the primary vibration to be unity, the expression for the scattered disturbance due to a single particle in a direction nearly coinciding with  $\theta=180^\circ$  is

$$\frac{A\lambda}{2\pi r} \cos \frac{2\pi}{\lambda} (ct - r - \delta)$$

where  $A$  and  $\delta$  determine respectively the amplitude and phase. The particles in the stratum are irregularly arranged, but in the direction of the primary wave propagation, the secondary waves diverging from the particles are in agreement of phase and can accordingly combine to build up a plane wave front. The amplitude and phase of this plane wave may be found by integration of the effects of the particles in the stratum in the manner adopted by Rayleigh in his paper on the theory of the light of the sky. Combining the effects due to causes (1) and (2) as discussed before, we have for the effect of passage of the wave through successive strata of the turbid medium

$$E = E_0 e^{-\left(2\pi\alpha^2 + \frac{A\lambda^2}{\pi} \sin \frac{2\pi\delta}{\lambda}\right) x} \quad \dots \quad (1)$$

where  $x$  is the total thickness traversed. (For details of the mathematical steps see Raman and Ray, Proc. Roy. Soc., Ser. A., Vol. 100).



### 3. *The colours of metal glasses and metal sols.*

In order to calculate the amplitude and phase of the secondary waves scattered in the direction of the primary wave, we utilise the formula given by Love as corrected by Rayleigh. In our present calculation we take the substance to be gold particles suspended in water, and we push our calculations for three wave-lengths

$$\lambda = 6300\text{A.U.}, \lambda = 5892\text{A.U.}, \text{ and } \lambda = 4584\text{A.U.}$$

The dielectric constant of the metal is a complex factor and is given by the relation

$$m = n^2(1 - ik)^2$$

where  $m$  = dielectric constant of the metal

$n$  = refractive index „

$k$  = absorption co-efficient „

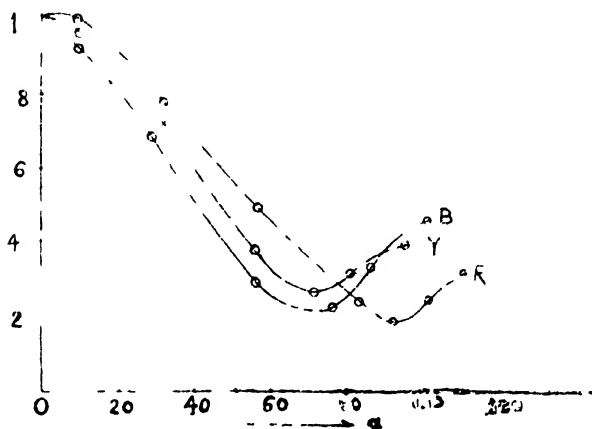
The proper value of the dielectric constant is substituted in the equations and calculations are made in the same way as done by the author previously. The value of  $n$  and  $k$  are different for different wave-lengths and the actual values are taken from Minor.

$\lambda$	$n$	$nk$
6300A.U	·31	3·15
5892A.U	·37	2·82
4584A.U	·79	1·52

Calculations are made for  $ka=1$ ,  $ka=2$ ,  $ka=3$ , and by drawing curves, the amplitude and phase of the scattered wave as a function of the ratio  $\frac{\text{circumference}}{\text{wave-length}}$  for gold particles in water for each of the wave-lengths  $\lambda=6300\text{A.U.}$ ;  $\lambda=5892\text{A.U.}$  and  $\lambda=4584\text{A.U.}$  can be obtained.

Since the process of integration considers the effect on the transmitted wave arriving at any given stratum of its passage through all preceding strata, the investigation takes

into account the influence of multiply-scattered light so far as is relevant to our present purpose.



The curve I is drawn showing

$$-\left(2\pi a^2 + \frac{\Lambda \lambda^2}{\pi} \sin \frac{2\pi \delta}{\lambda}\right) u$$

as ordinate and  $a$  as abscissa. From the graph it will be seen that the colour of the transmitted light is at first red and then it turns to yellow and finally blue. These results are in agreement with observation. In arriving at the equation (1) from the general expressions of Rayleigh (*l. c.*) we have taken that the spherical particles are without any limitations as to their refractive indices and to their radii as well, and we have assumed in these cases that the phases of the scattered waves arising from individual molecules are distributed entirely at random. We have further tacitly assumed that all the particles are of the same size. In the actual experiment, the size of the particles is variable to some extent, but by taking the effective average size, we may obtain a sufficient approximation to the truth; if desired there would be no difficulty in modifying the formula to obtain a more accurate result by

considering separately the effects of particles of different sizes in groups and superposing them to find the resultant.

In this case, the equation is true when the particles are fairly large (contrary to Garnett's assumption) and in the calculation we have considered gold particles in water. We can very easily substitute the value of the refractive index of glass for water in order to find the colours of gold glasses. Also substituting the refractive index of silver for gold in the previous calculation, the transmission colours of silver suspensions in water and also of the silver glasses can be obtained. The curve I gives the general explanation of the observed results.

#### 4. *Colours of aerosols.*

Barus has observed that the colour of the light transmitted through clouds of water, ether, and alcohol drops suspended in air undergoes periodic changes. Taking a typical case, say water, the axial colour is violet-blue when  $a=370 \times 10^{-6}$  c.m. With the increase in size of the particles, the colour changes from blue, green, yellow, red, purple, and violet-blue again when  $a=620 \times 10^{-6}$  c.m. and with still further increase in size, the axial colour changes from green, yellow, red, and violet again when  $a=790 \times 10^{-6}$  c.m. No explanation of these periodic changes of colours has yet been given. Recently Werner<sup>1</sup> has repeated this experiment with water drops alone, and measured the intensity of the transmitted light, keeping the number of particles per unit volume fixed, but gradually increasing the size. He has observed that, as the particles increase in size, the intensity gradually decreases till it is minimum and with further increase in the size, the intensity slightly increases but with still further increase in the size, it decreases again.

<sup>1</sup> Ann. der Phys., Vol. 70, 1923.

In order to explain the colours and also the oscillatory character of the intensity we examine the previous equation

$$E = E_0 e^{-\left(2\pi a^2 + \frac{A\lambda^2}{\pi} \sin \frac{2\pi}{\lambda} \delta\right) n}$$

and observe that as  $a$  increases both  $A$  and  $\delta$  increase, the value of  $2\pi a^2$  gradually increases and  $\sin \frac{2\pi}{\lambda} \delta$  passes also through maxima and minima, and hence the whole value of

$$-\left(2\pi a^2 + \frac{A\lambda^2}{\pi} \sin \frac{2\pi}{\lambda} \delta\right) n$$

shows an oscillatory character; also since the variation of the value of

$$\frac{A\lambda^2}{\pi} \sin \frac{2\pi}{\lambda} \delta$$

is small compared with  $2\pi a^2$ , it follows that the increase in intensity after passing through the first minimum though very small, is appreciable. This explains the general character of the phenomena observed by Barus and Werner. Further we know that  $Q = \frac{4}{3}\pi a^3 \cdot n$  where  $Q$  = water content of the vessel and  $a$  the radius of the particles and  $n$  the number of particles per unit volume, and if we substitute the value of  $n$  in the equation (1), and keep  $Q$  constant in the equation, we can express the intensity of the transmitted light in terms of the size of the droplets. The theoretical curves so drawn resemble the experimental values observed by Werner (*l.c.*)

### *Summary and Conclusion.*

In this paper, (a) the gradual changes of colour of the light transmitted through colloidal solutions, with the increase in the size of the particles, (b) the colours of the metal glasses, (c) the axial colours seen through the droplets of water, ether, alcohol, etc., have been examined. The intensity of the

light in passing through the medium is according to this procedure seen to be due to two causes.

(1) The decrease in the area, and consequently also of the resultant effect of the undisturbed portion of the wave front; and

(2) The interference with this light of the light scattered in the direction of the primary wave by the particles lying in the wave front.

By combining the resultant effect due to (1) and (2) we get

$$E = E_0 e^{-\left(2\pi a^2 + \frac{A\lambda^2}{\pi} \sin \frac{2\pi}{\lambda} \delta\right) n c}$$

where  $A$  and  $\delta$  are the amplitude and phase of the secondary waves which alter rapidly with the increase in the size of the particles. The second term within the bracket contains a sine factor which becomes alternately a maximum and a minimum when  $a$  increases and hence the value of  $E$  shows the oscillatory characters observed in the experiment. Since the values of  $A$  and  $\delta$  are functions of  $\lambda$ , the transmitted light becomes coloured.

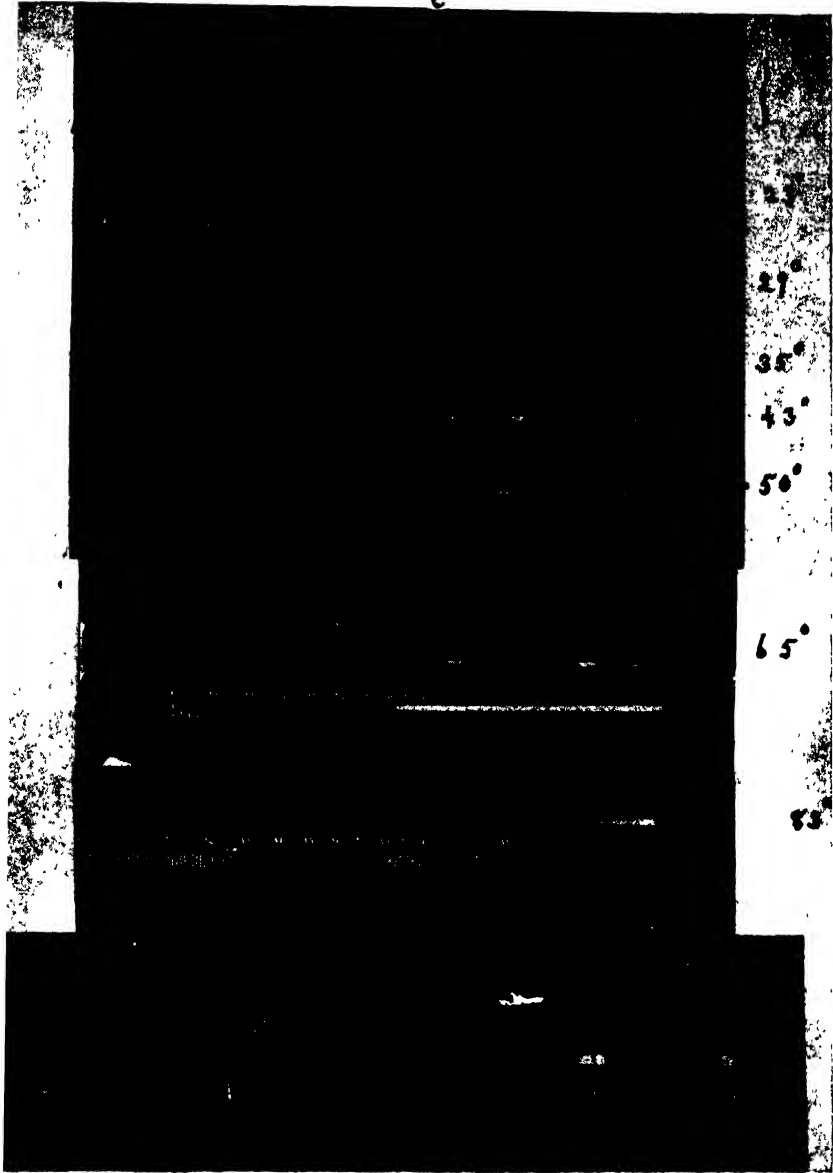
My thanks are due to Prof. C. V. Raman for his interest and helpful suggestions during the progress of the work.

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*Calcutta.*

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SPECTRA OF LIGHT REFLECTED BY CHLORATE OF POTASH

# XV. Colours of Chlorate of Potash.

BY

L. A. RAMDAS, M.A.,

*Palit Research Scholar in the Calcutta University.*

(Plate V.)

*Contents :*

- (1) Introduction.
- (2) Crystallisation of potassium chlorate.
- (3) Measurement of refractive index of potassium chlorate.
- (4) Spectrum of the reflected light.
- (5) Spectro-photometry of the reflected light and discussion of experimental results.
- (6) Conclusion.

## § 1. *Introduction.*

The remarkable reflection of light by certain crystals of potassium chlorate was first described by Stokes.<sup>1</sup> The late Lord Rayleigh<sup>2</sup> worked out a theory of the reflection of light at a twin plane of a crystal. Lord Rayleigh inferred that the reflection is from a large number of twin planes periodically situated. Wood<sup>3</sup> experimentally verified this fact by photographing the spectrum of the reflected light in which he got very narrow bands. In the case of one crystal the band was so narrow as to require 700 twin planes.

The presence of these twin planes was actually observed by Dr. Hodgkinson<sup>4</sup> in a specimen mounted in a special way. In this specimen the edges of the twin planes could be seen

<sup>1</sup> P. R. S., Feb., 1885.

<sup>2</sup> Phil. Mag., Vol. XXVI., 1888, pp. 241-265.

<sup>3</sup> R. W. Wood's Physical Optics, p. 160.

<sup>4</sup> Manchester Proceedings for 1889, Vol. III, p. 117.



by means of a hand magnifier. The present Lord Rayleigh<sup>1</sup> has in a recent paper given microphotographs of sections cut at right angles to the twin planes taken with crossed nicols. They clearly show the edges of the twin planes. Similar photographs have also been taken with Madan's crystals where the edges are not equally spaced. This confirms the late Lord Rayleigh's prediction.

In the present paper an attempt has been made to verify the late Lord Rayleigh's theory by spectro-photometry. The refractive index of the crystals has been measured for different wave-lengths for the first time by a simple method, exact calculation being impossible without a knowledge of these values. The conditions under which these crystals are formed have been studied with some care. Spectrum-photographs of the reflected light for different angles of incidence have been taken to study the variation of the width of the maxima with the angle of incidence.

## § 2. *Crystallisation of potassium chlorate.*

Pure and dust-free solutions of the salt do not yield any iridescent crystals. A few slightly coloured crystals are sometimes got. They are, however, of the type studied by the present Lord Rayleigh showing complex bands in the spectrum of the reflected light and having only a few twin planes very irregularly situated. They have none of the regularly repeated and innumerable twin planes which exist in the iridescent crystals. In solutions purposely made dirty many coloured crystals are always found. A large quantity of very clean solution was divided amongst five clean vessels. One of them was kept well covered and free from any disturbance. To three other samples small quantities of common salt, potassium chromate and fine dust were added. The remaining sample was attached to a pendulum and given

regulated shaking. The dusty solution gave a large number of iridescent crystals. The chromate solution also gave a few. The pure solution as well as the one containing common salt gave not even a single coloured crystal. The effect of the shaking was to precipitate the crystallisation. The crystals were formed too quickly to be large but there were innumerable thin crystals of the iridescent type. On the whole a suspended impurity like dust appears to be most effective in forming a large number of regularly arranged twin planes. Foreign matter seems to hinder the continuous and undisturbed growth of a crystal and help the formation of fresh layers which are either actually rotated through two right angles or in which the atoms are arranged in other positions of equilibrium corresponding to those of a crystal rotated through two right angles. The latter appears to be the more probable view.

In this connection it may be interesting to note that Madan's crystals are formed on heating one of the ordinary crystals to nearly its fusing point, when the amplitude of the atomic vibrations has nearly reached the maximum value which it can attain without breaking down the crystal structure, and then allowing it to cool. After the atoms have gained sufficient energy for them to assume alternative positions of equilibrium corresponding to those of a crystal turned through two right angles, they slowly come to rest on cooling and show the twinned structure which has been studied by both the late and the present Lord Rayleigh. The former has shown that the effect of heating is not to form actual cavities inside the crystal but to form twin planes as in the iridescent crystals. Spectrum-photographs of the reflected light and microphotographs of sections of Madan's crystals have been taken by the latter which show that the twinned structure is complex. It appears that twin crystals of Leucite ( $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ ), on heating, lose all traces of the twin planes which they had before, and are

converted into ordinary crystals on cooling. It would be interesting to study the structure of ordinary as well as inidescent crystals of potassium chlorate with the help of X-rays. No less interesting would be the study of the changes in the Laue patterns of an ordinary crystal on heating to nearly  $250^{\circ}$  and then allowing it to cool.

### § 3. *Refractive index of potassium chlorate.*

It was found that no data are available for the refractive indices of the crystal for different wave-lengths. They were determined by the following simple method.<sup>1</sup>

A fairly big-sized and thick crystal was attached to a pin with one of the edges vertical and it was immersed in a small quantity of carbon-disulphide contained in a cell with parallel glass windows. An illuminated slit was viewed through the cell keeping the edge of the crystal in a line with the eye and the slit and parallel to the latter. On turning the crystal about a vertical axis a position was found for which a well-defined spectrum was formed far away on one side of the slit. On carefully observing this spectrum it was found to consist of two spectra slightly separated from each other and polarised at right angles (vertically and horizontally). The spectrum nearer the slit was polarised with vibrations vertical.

The spectra had the red towards the slit. By adding benzol in suitable quantities the refractive indices for different colours were made equal both in the liquid mixture and in the crystal, beginning with the red. At each stage the particular colour for which the indices are equal coincides with the slit. The measurements were made only for the nearer spectrum. The refractive indices of the liquid

<sup>1</sup> "On Wave-propagation in Optically Heterogeneous Media and the Phenomena observed in Christiansen's Experiments." By Dr. Nihal Karan Sethi (Proc. Indian Association, Vol. VI, p 121)

mixtures were measured with the help of a Pulfrich Refractometer calibrated each time for the particular colour under consideration with the help of pure benzene and toluol whose refractive indices are known for different regions of the spectrum. For yellow light the sodium flame and for the other colours the light from a candle flame were used. The refractive index-wave-length graph was drawn so that the refractive index may be roughly ascertained for any wave-length. From two known values of the refractive indices for two wave-lengths Cauchy's constants were calculated so as to check the values obtained for other wave-lengths.

Table I.

Refractive index of  $\text{KClO}_3$ ,

COLOUR.	$\lambda \times 10^8$	$\mu$ (experimental)	$\mu$ (calculated)
Red	6500	1.529	
Yellow	5896	1.531	
Green	5000	1.539	1.537
Blue	4500	1.544	1.541
Violet	4000	1.549	1.547

$$\mu = A + \frac{B}{\lambda^2}$$

$$A = 1.518$$

$$B = 4.7 \times 10^{-11}$$

### § 1. Spectrum of the reflected light.

The coloured crystals were carefully selected from each crop, washed with a small quantity of distilled water, dried on filter paper and transferred to a card-board box. The light reflected from one of these crystals was found to be extremely interesting. There were two, and in some positions, three orders of maxima in the visible region of the spectrum, each maximum with secondary maxima (three in some cases) on either side. The repetition of the same structure in the various orders of maxima is the best evidence for the identity of their origin. The presence of the secondary maxima is exactly in accordance with the explanation put forward by

the late Lord Rayleigh. The present Lord Rayleigh has observed similar secondary maxima in the spectrum of the light reflected by "Pelidnota Sumptuosa."

The accompanying plate (Plate V, fig. 1) was taken with the bigger type quartz spectrograph of Adam Hilger (using panchromatic plates). It is very interesting to note how enormously the widths of the maxima decrease as they are made to travel from the violet towards the red end of the spectrum by decreasing the angle of incidence. Against each spectrum is marked the angle of incidence. Plate V, fig. 2, is a photograph of the spectrum taken with the carbon arc and it shows five orders in the blue, violet and ultra-violet (4th, 5th, 6th, 7th and 8th orders respectively). The positions of the maxima are marked. The photograph was taken with an ordinary plate and so the 3rd order in the red has not come out.

The co-efficient of reflection of a twin plane is zero at normal incidence and increases rapidly as the angle of incidence is increased, so that the effective number of twin planes reflecting (once the reflection has become total at about  $15^\circ$  angle of incidence) decreases rapidly in proportion. This readily accounts for the change in the width of the lines for different angles of incidence. With the aid of a travelling microscope the widths of the various orders of maxima as well as their wave-lengths were measured. It is evident that  $\frac{\lambda}{d\lambda} = n \times m$ , where  $n$  is the order of a band and  $m$ , the number of twin planes acting. In the present case it is justifiable to assume that each plane reflects only once as the distance  $t$  between two consecutive planes multiplied by  $m$  when the incidence is nearly normal (*i.e.*, when all the planes are contributing to the reflected light) is very nearly equal to the total thickness of the crystal.

$$m \times t = 35 \times 0.000664 = 0.023mm. \text{ (} t \text{ being calculated for a yellow band)}$$

$$m \times t = 35 \times 0.000670 = 0.0235mm. \text{ (} t \text{ being calculated for a blue band)}$$

The actual thickness measured by means of a microscope was about  $\cdot 025mm$ .  $n$  was calculated from the positions of the successive orders in one of the spectra, the refractive indices of the corresponding wave-lengths being known already. In the formula  $2\mu t \cos r = n\lambda$ ,  $r$ , the actual angle of incidence at the twin plane ( $r$  is the angle of refraction into the crystal) is different for different colours and  $t$  is calculated from a knowledge of  $\mu$ , the refractive index, and the angle of incidence at the external face of the crystal. The value of  $n$  was found to be 3, the three orders visible in most of the spectra in the plate being the 3rd, 4th, and 5th respectively.  $m$ , the number of planes acting was thus calculated for the wave-lengths corresponding to the three maxima in the spectra photographed.

The late Lord Rayleigh derived the following expression for the amplitude of the light reflected from a single twin plane:—

$$\eta = \frac{B}{2D} \frac{\sin \phi}{\cos^2 \phi}$$

where  $\eta$  is the co-efficient of reflection,  $B$ ,  $D$  the dielectric constants of the crystal and  $\phi$  is the angle of incidence at the twin plane. For the aggregate reflection from a series of twin planes ( $m$  in number).<sup>1</sup>

$$|\phi m|^2 = \tan h^2 m \beta_1$$

where

$$\beta_1 = \pm \tan h^{-1} \eta$$

or

$$\eta = \tan h \frac{\beta_1}{2}$$

when the light is totally reflected,  $\tan h^2 m \beta_1 = 1$ .

But

$$\eta = \frac{B}{2D} \frac{\sin \phi}{\cos^2 \phi} = \tan h \frac{\beta_1}{2}$$

Knowing

$\eta$  and  $\phi$ ,  $\frac{B}{2D}$  can be estimated.

The values are given in Table II.

Proc. Royal Society, No. A-655, Oct. 1917, "On the Reflection of light from a Regularly Stratified Medium."

Table II.

Measurement of the widths of the bands in the photographs, add the calculation of the number of plates reflecting and  $\eta$  are given below:—

$\theta$  = angle of incidence at the external face of the crystal.

$\phi$  = actual angle of incidence at twin plane = angle of refraction given by  $\sin \phi = \frac{\sin \theta}{\mu}$ .

$\theta$	$n$	$\lambda \times 10^{-8}$	$d\lambda$	$\frac{\lambda}{d\lambda}$	$m$	$m\theta_1$	$\frac{\beta_1}{2}$	$\eta = \tan h \frac{\beta_1}{2}$	$\frac{\sin \phi}{\cos \phi}$	$R = \frac{\eta}{2D \sin \phi / \cos^2 \phi}$
50°30'	3	5850	119.4	49	16		.156	.1541	.6748	.2284
	4	4500	112.7	40	10	5	.2500	.2451	.1670	.3656
	5	3670	95.08	38.63	8		.3125	.3028	.0666	.453
43°20'	3	6125	124.9	49.4	17		.1471	.1464	.2110	.2010
	4	4600	97.83	47	12	5	.2184	.2069	.5547	.731
	5	3771	74	51	10		.2500	.2450	.5507	.4449
35°36'	3	6130	138.3	51.99	18		.1389	.1381	.4134	.3116
	4	473	83.62	56.87	14	5	.1785	.1765	.4392	.4019
	5	3850	53.48	72.01	14		.1785	.1765	.4243	.4169
29°20'	3	6220	109	57.1	19		.1316	.1309	.3568	.3678
	4	4810	67.45	71.3	19	5	.1781	.1781	.3510	.3992
	5	3950	46.10	83.1	17		.1471	.1464	.5518	.4162
23°	3	6250	51.56	68	13		.186	.1881	.2752	.3460
	4	4850	68.34	71	18	5	.1381	.1381	.2713	.5091
	5	3900	44.36	90	18		.1389	.1381	.2678	.5121
4°	3	4900	37.34	130	37	5	.1676	.676	.0154	1.485
	5	460	26.35	153	31		.0833	.030	.0452	1.836

§ 5. *Spectro-Photometry.*

The photometric measurements were made by means of Hilger's Nutting Spectro-Photometer in series with an ordinary spectroscopè fitted with an adjustable slit in the focal plane of the eye-piece. The adjustable nicol of the photometer was set for complete extinction of the central spectrum, the reading in the graduated circle being then  $0^\circ$ . Thus if the reading is  $\theta$  when the spectrum is adjusted to be equal to the two spectra given by some other source,  $\sin^2 \theta$  gives the ratio of the intensities of the two sources compared. In a line with the aperture which gives two images a small spectrometer was adjusted so that the reflected light coming from the crystal mounted vertically on the prism table passes through the telescope deprived of its lens and eye-piece. The use of this additional spectrometer for the crystal is only to enable accurate measurement of the angle of incidence at the crystal face. The two sources were always kept at the same distance from the two apertures of the Nutting photometer. The ratio of the two sources was measured for different regions of the spectrum before calculating the correct reflecting power of the crystal. The two sources were a half-watt lamp and a 50 candle power electric bulb.

It is evident from Table II that for a given angle of incidence at the external surface of the crystal the value of  $\eta$  increases as the wave-length of the reflected light decreases; but in calculating  $\frac{\sin \phi}{\sin' \phi}$  we assume that B varies for different wave-lengths as indicated by the values of  $\frac{B}{2D}$  in the last column and that the reflection co-efficient  $\eta$  varies exactly as  $\frac{\sin \phi}{\cos' \phi}$ . It has to be borne in mind that the theory of Lord Rayleigh is not concerned with dispersion, but assumes that only light of a particular wave-length is incident on the crystal. On observing the spectrum of the transmitted light and increasing the angle of incidence from



zero to about  $30^\circ$  slowly it was found that the black band in the blue became completely black for a smaller angle of incidence than the minimum in the red. This is in agreement with the higher value of  $\eta$  for the shorter wave-length.

*Spectro-Photometric Measurements.*

Table III gives the variation of the intensity of the reflected light on rotating the crystal in its own plane, keeping the angle of incidence constant. Lord Rayleigh has remarked that it should vary as  $\sin^2\theta$  where  $\theta$  is the angle between the plane of incidence and the plane of symmetry of the crystal.  $\frac{\sin^2\theta}{\sin^2\phi}$  ought to be constant which it fairly is for large values of  $\theta$  (say greater than  $30^\circ$ ). The experimental difficulties are greater for smaller values of  $\theta$ .

*Table III.*

$\phi$  = reading of photometer.

$\theta$	$\phi$	$\sin^2\theta$	$\sin^2\phi$	$\sin^2\phi^1$ [for twin plane] alone.	$\frac{\sin^2\theta}{\sin^2\phi^1}$
0	$9^\circ 45'$	0	·0287	0	
$10^\circ$	$10^\circ 15'$	·0301	·0317	·0030	10·04
$20^\circ$	$13^\circ 30'$	·1169	·0545	·0258	4·53
$30^\circ$	$23^\circ 30'$	·2500	·1590	·1303	1·92
$40^\circ$	$83^\circ$	·4130	·2966	·2679	1·54
$50^\circ$	$40^\circ 15'$	·5866	·4175	·3888	1·51
$60^\circ$	$48^\circ$	·7499	·5524	·5237	1·43
$70^\circ$	$57^\circ$	·8831	·7034	·6747	1·31
$80^\circ$	$64^\circ 35'$	·9701	·8147	·7860	1·23
$90^\circ$	$70^\circ 30'$	1·0000	·8888	·8601	1·16

$$\sin^2\phi^1 = \sin^2\phi - \sin^2\phi(\theta=0)$$

where  $\sin^2\phi(\theta=0)$  = the reflection from the external surfaces alone.

For angles of incidence up to  $30^\circ$  there was no difficulty of adjustment. For smaller angles a mirror had to be used for reflecting the light to get the required angle of incidence. Corrections have been made for the light reflected by the external surface.

*Table IV.*

Intensity for different values of the angle of incidence.

$\theta$ .	Red.	Orange.	Yellow.	Green.	Blue.	Indigo.	Violet.
$66^\circ 15'$			·07947				·1389
$65^\circ$			·06695				·1447
$61^\circ 45'$			·09521				·1206
$54^\circ$			·1041				·1346
$45^\circ$	·1297					·2513	
$42^\circ 15'$	·0893				·1667		
$34^\circ 30'$	·0425				·0974		
$29^\circ 15'$	·0414				·0588		
$25^\circ 21'$					·0693		
$21^\circ 15'$				·0779			·0388
$16^\circ 45'$				·0681			
$7^\circ$				·0070			
$5^\circ$				·0021			

The above values are not absolute. They are only for comparison. The fractions in the Table are the ratio of the intensity of the reflection by the crystal to that of the comparison source.

#### § 6. Conclusion and Summary.

From the measurements given in Tables II and IV it is clear that interference effects prevent the measurement of  $\eta$  for

all angles of incidence for a definite wave-length. It is necessary to secure a crystal which is known for certain to have only a single twin-plane, in order to verify Lord Rayleigh's theory.

(1) In the present paper the cause of the formation of the iridescent crystals is experimentally found to be the presence of dust and other suspended or dissolved impurity.

(2) The variation in the reflection co-efficient with the angle of incidence has been calculated and also spectrophotometrically measured and it has been found that  $\eta$  varies with  $\lambda$ , being more for shorter wave-lengths.

(3) The variation of the intensity of reflected light when the crystal is turned in its own plane without altering the angle of incidence has also been measured experimentally.

(4) The refractive index of the crystal has been measured for different wave-lengths.

(5) Photographs of the spectrum of the reflected light have been taken showing clearly the presence of secondary maxima on either side of the central band, sometimes three in number and also showing the change in the width of the central maxima of the various orders as the angle of incidence is changed. It is found that with increasing angle of incidence the number of twin-planes which contribute appreciably to the observed effect rapidly diminishes.

In conclusion, I wish to state that the above work was carried on at the Indian Association for the Cultivation of Science while the author was in receipt of a research scholarship from that institution and that my best thanks are due to Prof. C. V. Raman, M.A., D.Sc., for his valuable help and advice.

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## XVI. On the Colours of Mixed Plates.

### Part IV

By

K. SESHAGIRI RAO.

In the third paper of this series<sup>1</sup> the consequences of the new theory advanced in the second paper to explain the phenomena shown by mixed plates had been worked out in detail and the results obtained have been shown to be in agreement with experiment. In this paper it is proposed to deal with some further studies of the phenomena including those of dry films.

#### *Intensity Distribution in the Halo.*

The detailed description of the phenomena has been given in the first paper. The remarkable feature of the phenomena is that though the bubbles vary in size and shape arbitrarily and are irregularly arranged in the film, the diffraction halo exhibits a regular structure consisting of a series of circular rings which are close together in the centre of the halo and wider apart in the margin, the number of rings depending only on the thickness of the film and its composition. The theory proposed is that these effects are due to the scattering of light from the laminar diffracting edges in the film. Owing to the action of surface tension, the edges are drawn inwards as a meniscus which in this particular case may be assumed to be semi-circular. The theory worked out on this basis shows that the scattered light consists of two

<sup>1</sup> Phil. Mag., March 1921, June 1921 and September 1921.

sets of dark and bright circular rings, the first set extending to large angles of diffraction and the second of inappreciable intensity except at the centre of the halo.

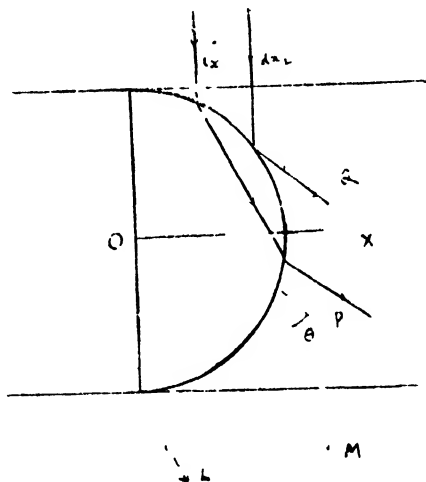


Fig. 1

The first is due to the interference of pencils P, Q and the other to the diffracted pencils L and M. The two sets of rings would be superposed on each other at the centre giving rise to the composite character of the halo. The position of dark rings in the first set is given by the angle of diffraction  $\theta$  where

$$\left. \begin{aligned} t\{1-\mu \sin i\} \{ \mu \cos i - \sqrt{1-\mu^2 \sin^2 i} \} - \delta = \\ (2n-1) \frac{\lambda}{2} \end{aligned} \right\} \dots \quad (1)$$

$$\mu \sin i = \sin r \text{ and } \sin \theta = \mu \sin 2(r-i)$$

$\delta$  = phase change occurring in total reflection depending upon the plane of polarisation of incident light.

The second set are determined by

$$(\mu-1)t + \frac{t}{2} \sin \theta - \frac{\lambda}{2} = (2n+1) \frac{\lambda}{2} \quad \dots \quad (2)$$

We shall now consider the relative intensity of the interfering pencils. The experimental observations already recorded show the interferences to be remarkably perfect and hence the interfering pencils must be of comparable intensity throughout the region in which we have maxima and minima.

That is what should be expected from considerations advanced above. In directions nearly normal to the film the light is diffracted chiefly from the wave fronts regularly transmitted through the film and the contributions to the scattered radiation from the part of the wave-front lying on either side of each boundary should obviously be equal. In more oblique directions the scattering occurs chiefly at the curved interface between the two media and the intensities of the pencils emerging respectively after two refractions and after total reflexion are comparable throughout. Thus there is reason to expect throughout the range in which scattered light can be observed the interferences to be strongly marked.

We shall now calculate the intensities of the two interfering pencils. Let the amplitude of the incident beam be unity. Let the two initial parallel pencils of width  $dx_1$  and  $dx_2$  give rise to the two interfering pencils lying between  $\theta$  and  $\theta + d\theta$ . The intensities of the two beams will be proportional to  $dx_1$  and  $dx_2$ .

$$\begin{aligned} \text{Now} \quad \frac{dx_1}{d\theta} &= \frac{a \cos i \, di}{2(\bar{dr} - \bar{di})} \\ &= \frac{a}{2} \frac{\cos i \cos r \sin i}{\sin r - i} = P_1 \end{aligned}$$

$$\text{and} \quad \frac{dx_2}{d\theta} = \frac{a}{2} \sin(r - i) = P_2$$

where  $a$  = radius of the semicircular edge.

The amplitude of the refracted pencil  $A_1$  is given by  $\left(\frac{P_1}{R}\right)^{\frac{1}{2}}$  where  $R$  is the distance of the point of observation. Similarly the reflected beam  $A_2$  is given by  $\left(\frac{P_2}{R}\right)^{\frac{1}{2}}$ . It will be evident from above that while  $A_1$  decreases as  $\theta$  increases  $A_2$  increases. In the case of the refracted beam we have to take into consideration the fact that all the light is not completely refracted but part is also reflected. The correction factor is given by Fresnel's co-efficient of refraction

$$\frac{\sin^2 i \sin^2 r}{\sin^2(i+r)} \text{ and } \frac{\sin^2 i \sin^2 r}{\sin^2(i+r) \cos^2(i-r)}$$

for components polarised respectively in the plane of incidence and at right angles to it. This will modify  $A_1$  very slightly at first but becomes appreciable at larger angles. We have also to consider the diffraction effect of the edge at  $O$  which will be very large for small obliquities but becomes quite negligible at larger angles. This effect might be considered as that due to another ray superposed on the direct rays. The expression for this will be given by Sommerfeld's expression for the diffracted wave at a semi-infinite screen, *i.e.*, by

$$\frac{1}{4\pi} \sqrt{\frac{\lambda}{R}} \left\{ \frac{1}{\cos \frac{\phi+\phi'}{2}} - \frac{1}{\cos \frac{\phi+\phi'}{2}} \right\} \\ \times \cos \frac{2\pi}{\lambda} \left( r - ut + \frac{\pi}{4} \right)$$

where  $\phi$  and  $\phi'$  are the angles made by the diffracted and incident beams with  $OX$  respectively.

The amplitude of this beam  $A_3$  is given by

$$\frac{1}{4\pi} \sqrt{\frac{\lambda}{R}} \left\{ \frac{1}{\cos \frac{\theta}{2}} - \frac{1}{\sin \frac{\theta}{2}} \right\} \text{ since } \phi = \frac{3\pi}{2} - \theta$$

and

$$\phi' = \frac{\pi}{2}$$

or by

$$\frac{1}{2\pi} \sqrt{\frac{\lambda}{R}} \frac{1}{\theta} \quad \text{when } \theta \text{ is small.}$$

In calculating the amplitude of the resultant the path difference between this and the reflected beam may be neglected. The path difference between the reflected and the twice refracted beams is given by (1). The resultant intensity is obtained by compounding the three beams. The effect due to  $A_3$  vanishes at moderately large angles.

The curve in the figure has been drawn on the above calculations. The asymptotic expansion

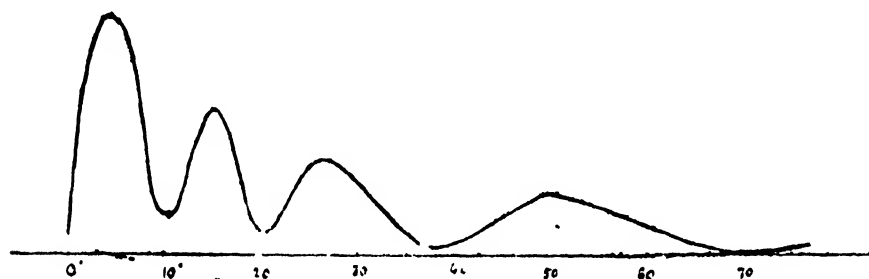


Fig. 2

of  $A_3$  is inapplicable over a small range near  $0^\circ$  and that part of the curve (from  $0^\circ$  to  $2^\circ$ ) has been drawn freehand so as to represent as closely as possible the trend of the curve. In the calculation  $(\mu-1)t$  has been taken as  $5\lambda$ .

It will be seen that the general features of the phenomena are well represented by the curve.

We have also to consider the second set of rays LM which are diffracted from the regularly transmitted wave fronts. The amplitudes of both of these will be equal throughout and hence the interferences will be perfect. But as the amplitude diminishes very greatly with moderately large angles its effect will be only seen for small angles. As will be seen from (1) and (2) the two curves will get out of



step at small angles the maximum of one coinciding with the minima of the other, the result being the blurring of the rings which is actually observed.

*Position of Achromatic Ring.*

The expression for the path-difference of the two interfering pencils given in (1) shows that it diminishes continuously (at first rather rapidly and later more slowly) from  $(\mu-1)t$  up to a small fraction of it for the largest angles of diffraction. We have accordingly a series of circular rings in the halo closer together at the centre and wider apart near the margin. The value of  $\delta$  diminishes gradually from  $\frac{\lambda}{2}$  to 0 as  $\theta$  increases. The outermost ring therefore in white light corresponding to a negligibly small path-difference should be achromatic while the inner ones should be strongly coloured. Near the centre of the halo the colours will not of course be pure. To investigate the exact sequence of colours and to determine whether the achromatisation of the last ring is perfect we have of course to take into account the variation of refractive index  $\mu$  with wave-length  $\lambda$ . The condition of achromatism is that the path-difference  $\Delta$  divided by  $\lambda$  should be independent of  $\lambda$ .

The path-difference  $\Delta$  is given by (1)

$$\Delta = 2\mu a \left\{ \cos i - \sin r - i \right\} - 2a \cos r - \delta$$

Achromatisation will be perfect when

$$\frac{d}{d\lambda} \left( \frac{\Delta}{\lambda} \right) = 0, \text{ i.e., } \lambda \frac{d\Delta}{d\lambda} = \Delta$$

now ,

$$\frac{d\Delta}{d\lambda} = 2a \left\{ \frac{d\mu}{d\lambda} (\cos i - \sin r - i) - \left( \mu \cos r - i - \sin r \right) \frac{dr}{d\lambda} \right\} \text{ approximately}$$

since

$$\frac{dr}{d\lambda} = \frac{d\mu}{d\lambda} \frac{\sin i}{\cos r}$$

$$\frac{d\Delta}{d\lambda} = \frac{2a}{\cos r} \frac{d\mu}{d\lambda} \left\{ \cos r - i - \sin 2r - i \right\}$$

Assuming  $\mu$  to be given by Cauchy's formula

$$\mu = A + \frac{B}{\lambda^2}, \quad \frac{d\mu}{d\lambda} = -\frac{2B}{\lambda^3}$$

Hence the condition of achromatisation is given by

$$\begin{aligned} & \frac{d\mu}{d\lambda} \frac{\lambda}{\cos r} \left\{ \cos r - i - \sin 2r - i \right\} \\ &= \mu \left\{ \cos i - \sin r - i \right\} - \cos r \end{aligned}$$

Assuming  $\mu$  and  $\frac{d\mu}{d\lambda}$  to be the same as that for water we find this condition is satisfied when  $i$  is about  $40^\circ$ , i.e., when  $\theta$  is about  $90^\circ$ . We thus find that the achromatism of the last ring is nearly perfect.

### *Dry Films.*

The phenomena exhibited by dry or partially dry films have been described in detail in the first paper of the series. Briefly described it consists of a halo which is much *fainter* than in the case of fresh films showing a broad central area which is achromatic followed *outside* by rings of gradually decreasing width which are strongly coloured. The diffraction halo in fact is very similar to the wellknown diffusion rings observed around the focus of a thick concave mirror with a dusted surface. The resemblance also extends to the case in which the plate is held obliquely in front of the eye. As the plate is inclined, the centre of the halo moves to one side, fresh fringes appearing on that side, and ultimately, as the

plate is held at a moderate obliquity, the halo consists of only arcs of circles, the arc passing through the source being achromatic, the rest being coloured in white light. The explanation of this becomes clear when we understand how drying affects the film. As has been already described, the bubbles of air in the film which are at first lying indiscriminately are drawn together leaving the albumen confined to a number of very fine ridges, the form of these ridges being that of irregular hexagons. In the dry film it is these ridges that form the diffracting centres. The case then becomes similar to diffraction by small particles on the surface of a mirror. If

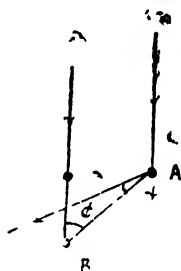


Fig. 3

A and B be the two diffracting particles and if  $\phi$  be the angle which the direction of the incident light makes with AB and  $\psi$  the angle of diffraction it can be easily shown that the positions of maxima and minima are given by

$$t(\cos \phi - \cos \psi) = m \frac{\lambda}{2}$$

or for small angles

$$\psi^2 - \phi^2 = \frac{m\lambda}{t},$$

odd values of  $m$ , 1, 3, etc., giving the minima.

To test these conclusions the angular diameter of the rings was measured using a monochromatic light source. A small aperture illuminated by a mercury lamp with a green filter forms the source of light. It is viewed through the

film formed between thick flat plates. The angular width of the dark rings in the halo may be determined by making them coincide in succession with a faint luminous reference mark placed in the same plane as the source, the plate being moved in the direction of the incident light. The thickness of the film was determined by observing the spectrum of white light transmitted through the film and noting the wave-lengths of the light freely transmitted through the film without interference.

Results of a few observations are given below.

Thickness of film  $t=9\lambda$ .

Observations in the normal case when  $\phi=0$ .

Number of ring $n$	Angle $\psi$ (in degree)	$\frac{\cos \phi - \cos \psi}{n}$
1	18° 10'	0.050
3	31° 0'	0.048
5	40° 36'	0.048
7	50° 0'	0.051

Observations when  $\phi=9^{\circ}30'$

Number of ring $n$	Angle $\psi$	$\frac{\cos \phi - \cos \psi}{n}$
1	19° 30'	0.045
3	30° 30'	0.042
5	42° 0'	0.048

It is worth while recording another feature exhibited by the dry films. As already described the dry film when held at normal incidence shows a series of circular

rings as shown in the drawing Fig. 4(i). When tilted the

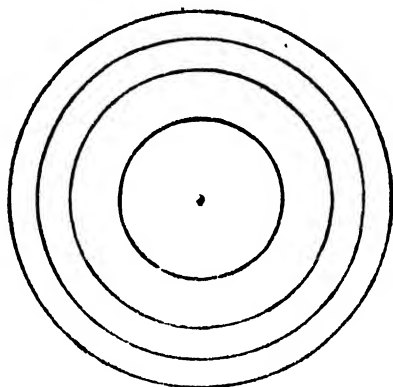


Fig. 4(i)

centre of the halo moves to one side fresh fringes appearing on that side, the rings remaining approximately circular as in the case of Newton's rings. When closely examined it is found that when the plate is tilted, besides these circular rings there appear another set of rings cutting the former rings and moving in an opposite direction. At the place where these cut the first set of rings there is present a dislocated appearance. The first set of rings appear displaced at these points, and appear to be slightly bulging at one side. The rings are very faint. Appearance of these rings is shown in the diagram Fig. 4(ii). When the plate is very obliquely

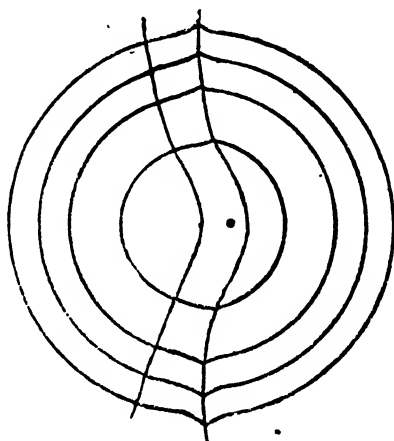


Fig. 4(ii)

held the two sets appear to merge and only arcs of circles are seen as in the case of Newton's diffusion rings. This is shown in Fig. 4(iii). The nature of the second set of rings is not yet

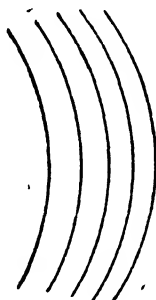


Fig. 4(iii)

clear. As already described the film when dry forms into a network of polygonal ridges. It is possible that the peculiar structure of the film may cause the appearance of this second set of rings.

#### *Summary.*

(1) In this paper the intensity distribution of the halo exhibited by the mixed plate is studied and explained.

(2) The position of the achromatic ring has been determined.

(3) The phenomena exhibited by dry films has been shown to belong to the class of Newton's diffusion rings by quantitative measurements.

In conclusion the author has much pleasure in recording his best thanks to Prof. C. V. Raman.

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# The Opalescence of Binary Liquid Mixtures

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## PART I. EXPERIMENTAL.

### 1. Introduction.

While making a systematic study of the mutual solubility of liquids, Alexejew,<sup>1</sup> Guthrie<sup>2</sup> and Rothmund<sup>3</sup> were the earliest to note that certain pairs of liquids, *e.g.*, phenol and water, isobutyric acid and water, hexane and methyl alcohol,

<sup>1</sup> Wied. Ann. 28, p. 305 (1886).

<sup>2</sup> Phil. Mag. (5) 18, p. 504 (1884).

<sup>3</sup> Zeit. Phys. Chem. 26, p. 433 (1898).

„ „ 63, p. 54 (1908).



above a certain temperature called the critical solution temperature are perfectly miscible and form a single phase but below which are only partially soluble and divide into two co-existent phases. They also found that such mixtures exhibit a marked opalescence or turbidity at a temperature slightly higher than that at which they separate into two layers. As their primary object was the study of mutual solubility of mixtures, their observation was restricted to the observation of the phenomenon of critical opalescence. Further work on the subject was done by Konowalow<sup>1</sup> who investigated the connection between the opalescence and variations in the partial vapour pressures, these variations being the most important criterion of solution. The results which he obtained for solutions of aniline and amylene in the critical range showed a similarity between these and colloidal solutions, the dependence of the vapour pressure on the concentration of the solutions being very small. He finally adopted the view that the opalescence of liquids is due to dust and that the increased opalescence in the critical range is due to the greater facility with which the components separate in this region and condense on the dust nuclei. As we shall see later, this conclusion of Konowalow is not true, as the opalescence is obtained even in the case of dust-free liquids. So far the observations were more or less of a qualitative nature, no attempt having been made to observe the amount of light scattered by the liquid mixtures.

It was after Smoluchowski<sup>2</sup> and Einstein<sup>3</sup> gave a theory to explain the critical opalescence of liquid mixtures, that quantitative measurements were made by Fürth<sup>4</sup> for the mixtures of phenol and water and Zernike<sup>5</sup> for the mixtures

<sup>1</sup> Ann. der. Phys. 10, p. 360 (1903).

<sup>2</sup> Ann. der. Phys. 25, p. 205 (1908).

<sup>3</sup> " " 33, p. 1275 (1910).

<sup>4</sup> Wiener Berichte, 124, p. 577 (1915).

<sup>5</sup> Thesis Amsterdam (1914).

of methylene iodide and penta methylene, nitrobenzene and diisobutyl. Their observations were however restricted only to a short range of temperature above the critical temperature, for which the theory was intended. More recently Martin and Lehrman<sup>1</sup> made some interesting observations regarding the intensity and state of polarisation of some mixtures of liquids which are completely miscible at ordinary temperature, *viz.*, carbon bisulphide and ether, benzene and normal hexane and normal hexane and cyclo hexane. As it was not the aim of the above authors to verify any theory but simply to observe the variation of intensity and polarisation of the scattered light for various concentrations of the mixtures, they chose some arbitrary pairs of liquids. As will be seen later from the theoretical part, partial vapour pressures and compressibilities of mixtures are necessary for the verification of the theory and unfortunately such data are not available for the pairs of liquids studied by Martin and Lehrman. V. S. Tamma, working at Calcutta, made a study of the scattering of light by mixtures of phenol and water for a range of 30°C above the critical solution temperature. He found the intensity of the scattered light to be very large and almost completely polarised in the immediate neighbourhood of the critical temperature and as the temperature is increased the intensity diminishes and the scattered light is less perfectly polarised. The present author<sup>2</sup> has studied the intensity of scattering and the state of polarisation of mixtures of carbon bisulphide and acetone. Following up this work the author has carried out a series of observations with mixtures of toluene and acetic acid at the room temperature and with mixtures of methyl alcohol and carbon bisulphide at temperatures both above and below the critical solution temperature, the results of which are now set out.

<sup>1</sup> Jour. Phys. Chem., 26, p. 75 (1922).

<sup>2</sup> Physical Review, July 1923. Hereafter this will be referred to as paper A.

## 2. *Technique of observation and measurement.*

The chief difficulty in the work is to prepare perfectly dust-free liquids. To achieve this end, slightly different forms of apparatus are used for the wholly miscible liquids and partially miscible ones. For the former, the mixtures are contained in cut glass bottles having flat sides and are rendered dust-free in the same manner as that described in paper A. Five different mixtures of toluene and acetic acid of different concentrations are prepared.

Though distillation in bottles is found to be very convenient for accurate measurements of intensity and polarisation at ordinary temperatures, at higher temperatures either the joints no longer remained tight with the result that leakage ensued or the bottles are not found to be strong enough to resist the large internal pressure. Thus for the study of scattering by mixtures of methyl alcohol and carbon bisulphide (a case of partially miscible liquids), at different temperatures the apparatus used is similar to that used by Raman and Seshagiri Rao.<sup>1</sup> The apparatus consists simply of two bulbs connected together containing the mixture and the air inside is exhausted to facilitate distillation. The liquid is distilled from one bulb to the other. After repeating the operation five or six times the bulb containing the liquid is sealed off. Three bulbs containing respectively 25, 50 and 75 per cent. of carbon bisulphide by volume are prepared.

For measurements of the intensity of scattered light, a second bottle containing toluene is used as a standard of comparison in all cases. The measurements are made in the same manner as described in paper A, the only difference being that in the case of mixtures of toluene and acetic acid, the two bottles are set closely side by side with a uniform film of glycerine between them, to ensure against any loss of light by reflection at the surfaces. To get more accurate results the bottles are interchanged, the relative intensity is noted

<sup>1</sup> Phil. Mag., Mar. 1923, p. 625.

again and the mean value is then taken. In the case of mixtures of methyl alcohol and carbon bisulphide the bulb is immersed in a rectangular glass vessel having flat sides and containing clear distilled water. The glass sides are painted jet black outside, openings being left for admission and exit of the beam of light passing through the liquids. For the small thicknesses of the liquids used, the effect of the absorption of light is quite negligible. Indeed the colour of the tracks observed in the pure liquids and mixtures was found to be blue and no difficulty was experienced in making the intensity measurements. Care is taken to see (especially in the case of bulbs), that the liquids are exposed only for a short time to avoid any decomposition of the liquid when observations are taken.

Polarisation measurements are made as in the previous case by a double image prism and nicol. The double image prism gives two images of the track polarised respectively in horizontal and vertical planes. By rotating the prism the two images can be brought into a line. By rotating the nicol placed immediately behind the prism, two positions may be found in which the images appear of equal intensity. If  $2\theta$  be the angle between these positions of the nicol, then  $\gamma = \tan^2 \theta$ , where  $\gamma$  is the ratio of the weak component to the strong.

### 3. *Results with wholly miscible liquids.*

The observed intensities for mixtures of toluene and acetic acid for different concentrations are given in the following table. As was stated before, Toluene is taken as the standard. The results refer to 30°C.

TABLE I.

Liquid.	Toluene.	A.	B.	C.	D.	E.	Acetic Acid.
Percentage volume of toluene ...	100	83.3	66.7	50	33.3	16.7	0
Observed intensity ...	1.0	1.05	1.0	1.0	0.78	0.70	0.50

For the same pair of liquids the ratios of the weak component to the strong, of polarisation are given in the following table :

TABLE II.

Liquid.	Toluene.	A.	B.	C.	D.	E.	Acetic acid.
Percentage volume of toluene ...	100	83·3	66·7	50·0	33·3	16·7	0
$\theta$	36·6	34·3	31·6	30·2	29·7	32·8	37·4
100 $\gamma$	55	46·5	37·8	33·8	32·8	41·6	58·5

#### 4. Results with partially miscible Liquids.

The observed values of intensity for mixtures of methyl alcohol and carbon bisulphide for different concentrations and temperatures are given in the following table. In this case also toluene is taken as the standard. When the temperature is lowered the concentrations of the two layers in the bulbs alter. Intensities corresponding to these temperatures and concentrations are also included.

TABLE III.

Liquid.	Percentage volume of CS <sub>2</sub> .	OBSERVED INTENSITY.				
		$t = 20^{\circ}\text{C.}$	$t = 30^{\circ}\text{C.}$	$t = 40\cdot5^{\circ}\text{C.}$	$t = 50^{\circ}\text{C.}$	$t = 60^{\circ}\text{C.}$
CH <sub>3</sub> OH	0	0·08	0·08	0·1	3·1	0·33
A	25	0·72	0·74	0·92	1	1·1
B <sub>1</sub>	40	5·0	...	...	...	...
B <sub>2</sub>	48	.	6·5	...	..	...
B	50	...	..	23	14·5	6
C	75	..	...	80	16	9
CS <sub>2</sub>	100	1·5	1·6	1·75	1·75	2

For the same pair of liquids the polarisation measurements for different concentrations and temperatures are given in the following table :

TABLE IV.

Liquid.	Percentage volume of CS <sub>2</sub> .	100 $\gamma$ OBSERVED.				
		$t=20^{\circ}\text{C.}$	$t=30^{\circ}\text{C.}$	$t=40\cdot5^{\circ}\text{C.}$	$t=50^{\circ}\text{C.}$	$t=60^{\circ}\text{C.}$
CH <sub>3</sub> OH	0	9·5	9	9	9	9
A	25	20·3	20·0	16·3	22·5	23
B <sub>1</sub>	40	10	...	..	...	...
B <sub>2</sub>	48	..	6	...	...	...
B	50	...	...	5·1	7	10
C	75	...	...	3	4·6	18
CS <sub>2</sub>	100	70	70	70	69	69

To have a clearer idea of the variation of intensity and polarisation with temperature the following tables are given for the scattering in the two layers of bulbs A and C which contain respectively 25 and 75 per cent. of carbon bisulphide. In the latter case, two layers were present till about 40°C, beyond which the boundary line disappeared :

#### LIQUID A.

TABLE Va.

Temperature.	14	20	26	40·5	50	60
Intensity...	0·71	0·72	0·74	0·92	1·00	1·33

#### LIQUID C.

TABLE Vb.

Temperature in °C.	8	11	20	30	40·5	50	60
Intensity for upper layer	3	3·3	5	6·5	80	16	9
Intensity for lower layer	2	5	8	...	...	...	...

The above tables show very interesting variation of intensity with concentration and temperature. In the case of liquid A, where there is only a small percentage of  $\text{CS}_2$  the mixture behaves like a pure liquid—the intensity increasing continuously with temperature. On the other hand liquid C which at the critical temperatures contains nearly 75 per cent. of  $\text{CS}_2$  behaves in quite a different way. The intensity increases with temperature for both the layers till the critical temperature is reached, when it becomes enormous and beyond which the intensity begins to diminish.

The polarisation measurements also show a similar interesting variation. For the first mixture A, the variation with temperature is very small but at the critical temperature however,  $\gamma$  is a minimum. For the other mixture, the scattered light is almost completely polarised at the critical point but for higher and lower temperatures, the polarisation tends to become more and more imperfect. This is shown by the following tables.

#### LIQUID A.

TABLE VIa.

Temperature	10	15	20	30	40	50	60
$100\gamma$	23	21.5	20.3	20	16.3	22.5	23

#### LIQUID C.

TABLE VIb.

Temperature.		8	12.5	20	30	40.5	50	60
$100\gamma$ for upper layer	...	24	20	10	6	3	4.6	10
$100\gamma$ for lower layer	...	46	19	...	...	...	...	...

## PART II. THEORETICAL.

I. *Introduction.*

As was mentioned in the introduction to Part I, the theory of the opalescence of liquid mixtures near the critical solution temperature was supplied by Smoluchowski and Einstein. These authors regarded the opalescence in liquid mixtures as due to local fluctuations of composition and consequent optical inhomogeneity. Einstein's theory of liquid mixtures is intended to explain only the scattering of light in a small range of temperature above the critical solution temperature and is based on the following assumptions—that the liquids are incompressible, that their specific volumes are negligibly small in comparison with those of the saturated vapours emitted by them and that the latter can be treated as ideal gases; and on this basis he arrived at a formula for the opalescence of the mixture in terms of experimentally determinable magnitudes, namely, the variation of its refractive index and of the partial vapour pressure of its components with the alteration of concentration measured by the ratio of the mass of the second component to that of the first. This theory was verified for a small range above the critical temperature by Fürth and Zernike. The latter worked out also a theory based on statistical mechanics and arrived at a more general result, but in the end without making any calculations rejected the additional factors and finally arrived at Einstein's formula.

In a letter to *Nature*, C. V. Raman<sup>1</sup> drew attention to the limitation of Einstein's theory and showed that in the case of liquids which are completely miscible in all proportions at the ordinary temperature and in the case of partially miscible liquids at temperatures higher than the critical temperature, there are other factors, which must be taken into consideration, *e.g.*, molecular scattering of light due to density fluctuations of the liquid mixture and to the varying

<sup>1</sup> *Nature*, July 1922, p. 77.



orientations of the anisotropic molecules. This latter factor accounts for the large amount of unpolarised light in liquids scattered transversely to the primary beam. A fuller theory taking these factors into account was given by Raman and Ramanathan,<sup>1</sup> who showed that the experimental results could thus be satisfactorily explained.

In this paper an attempt is made to develop a theory of scattering of light by liquid mixtures, on the lines of Ramanathan's work for the case of pure liquids.<sup>2</sup> In article 2, the medium is assumed to be continuous as in Einstein's treatment of the subject, but subject to local fluctuations of density and concentration of the mixture depending on the laws of statistical mechanics. Lorentz's electromagnetic treatment of the scattering of light in gases has been adopted and extended to the case of liquid mixtures. In article 3, the subject is treated from the molecular standpoint in the case when the molecules are isotropic and the formula of Raman and Ramanathan for scattering by liquid mixtures is deduced. In article 4, the treatment is extended to the case when the molecules are anisotropic and a formula is developed for the intensity of scattered light.

## 2. *Continuous medium theory.*

Let  $\epsilon$  be the value of the mean dielectric constant of a medium when the distribution of matter is uniform and  $\epsilon + \delta\epsilon$  its actual value at a volume element  $\delta v$ . In a liquid mixture, owing to thermal movements the density of the mixture taken as a whole and the concentration of one liquid in the other undergo incessant fluctuations; consequently the dielectric constant of the mixture also.

Using Heaviside's absolute units, the dielectric displacement

$$D = \epsilon E \quad \dots (1)$$

<sup>1</sup> Phil. Mag., Jan. 1923, p. 213.

<sup>2</sup> Proc. Ind. Assoc. Cult. Science, Vol. VIII, p. 1.

where  $E$  is the electric intensity. When the density and concentration of the mixture are uniform, there would be no scattering of light, for the disturbances from different elements would mutually cancel each other except in the direction of primary propagation. At a place where the dielectric constant is  $\epsilon + \delta\epsilon$  the dielectric displacement

$$D_1 = (\epsilon + \delta\epsilon)E \quad \dots (2)$$

The discontinuity of displacement can be annulled by introducing a supplementary electric intensity

$$F = -\frac{\delta\epsilon}{\epsilon} E \quad \dots (3)$$

The scattering is thus identical with the radiation due to a system of electric intensities  $-F$  or  $\frac{\delta\epsilon}{\epsilon} E$  at the places where the dielectric constant differs from its mean value  $\epsilon$  by  $\delta\epsilon$ .

Suppose we have a volume element  $\delta v$  at the origin of co-ordinates where the dielectric constant is  $\epsilon + \delta\epsilon$ . When the linear dimensions of the element are small in comparison with the wave length, the amplitude of the disturbance from the element would be proportional to  $\frac{\delta\epsilon}{\epsilon} E \delta v$  and hence its energy is proportional to

$$\left( \frac{\delta\epsilon}{\epsilon} \right)^2 E^2 (\delta v)^2 \quad \dots (4)$$

In the case of scattering by a single volume element  $\delta v$

$$F = -\frac{\delta\epsilon}{\epsilon} E$$

and the ratio of the light radiated by the doublets to  $E^2$  the square of the amplitude can be shown to be

$$\frac{\sin^2 \theta}{r^2} \left( \frac{2\pi}{\lambda_1} \right)^2 \left( \frac{\delta\epsilon}{\epsilon} \right)^2 \frac{(\delta v)^2}{16\pi^2} \quad \dots (5)$$

where  $\lambda_1$  is the wave length of the incident vibration in the medium and  $\theta$  is the angle between the direction of the ray and axis of Z (the direction of the applied electric intensity).

Let us now consider the scattering produced by the accidental deviations of density and concentration in an extended volume. Let us take the X-axis to be the direction of the primary beam. The density and concentration deviations would change both in magnitude as well as in position in a perfectly arbitrary manner and there would be no co-ordination of phase between the vibrations scattered by the various elements. As a consequence, over any finite interval of time, the energies and not the amplitudes of the scattered radiations from the different elements of volume would be additive. If  $\delta\rho$  and  $\delta k$  denote the deviations of density and concentration from their mean values  $\rho_0$  and  $k_0$  in a volume element  $\delta v$  then we can easily show by Boltzmann's principle of entropy probability that the mean squares of deviations of density and concentration are given by <sup>1</sup>

$$\overline{(\delta\rho)^2} = \frac{RT\beta}{N\delta v} \rho_0^2 \quad \dots (6)$$

$$\overline{(\delta k)^2} = \frac{1}{\pi^2 N\delta v} \frac{M_2}{m_1} \frac{\partial}{\partial \log p_2} \frac{\partial}{\partial k} \quad \dots (7)$$

and

$$\bar{\delta\rho} \bar{\delta k} = 0 \quad \dots (8)$$

where R is the gas constant, T is the absolute temperature,  $M_2$  is the molecular weight of the second component in the gaseous phase,  $m_1$  mass of the first component in unit volume of the mixture,  $p_2$  is the partial vapour pressure of the second component,  $\phi$  is the compressibility of the mixture.

Now

$$\delta\epsilon = \frac{\partial \epsilon}{\partial k} \delta k + \frac{\partial \epsilon}{\partial \rho} \delta \rho$$

$$\overline{(\delta\epsilon)^2} = \left( \frac{\partial \epsilon}{\partial k} \right)^2 \overline{(\delta k)^2} + \left( \frac{\partial \epsilon}{\partial \rho} \right)^2 \overline{(\delta \rho)^2} \quad \dots (9)$$

<sup>1</sup> Einstein. Ann. der Phys., Vol. 33, 1910, p. 1275, also C. V. Raman and Ramanathan, Phil. Mag., Jan. 1923, p. 213

The relation between density and dielectric constant is given by Lorentz's formula, considering a mixture as a whole,

$$\frac{\epsilon-1}{\epsilon+2} \cdot \frac{1}{\rho_0} = \text{constant}$$

Hence

$$\frac{\partial \epsilon}{\partial \rho} = \frac{(\epsilon-1)(\epsilon+2)}{3\rho_0}$$

$$\left( \frac{\partial \epsilon}{\partial \rho} \right)^2 (\delta \rho)^2 = \frac{(\epsilon-1)^2 (\epsilon+2)^2}{9\rho_0^2}$$

and by (6)

$$= \frac{(\epsilon-1)^2 (\epsilon+2)^2}{9} \frac{RT\beta}{N\delta v}$$

Substituting in (5) the value of  $(\delta \epsilon)^2$  from (9) with the help of (6) and (7), we get for the ratio of the average intensity of the scattered radiation to that of the incident

$$\left[ \frac{\pi^2}{9} RT\beta (\epsilon-1)^2 (\epsilon+2)^2 + \frac{M_2}{m_1} \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_s / \partial k} \right] \frac{\sin^2 \theta}{N\epsilon \lambda_1^4 r^2} \delta v$$

Since the radiations from different volume elements are additive the above becomes

$$\left[ \frac{\pi^2}{9} RT\beta (\epsilon-1)^2 (\epsilon+2)^2 + M_2 \frac{1}{m_1} \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_s / \partial k} \right] \frac{\sin^2 \theta}{N\lambda^4 r^2} \dots \quad (11)$$

per unit volume where  $\lambda$  is the wave length of the incident vibration in vacuo.

In a direction at right angles to the primary incident beam, the above expression becomes

$$\left[ \frac{\pi^2}{9} RT\beta (\epsilon-1)^2 (\epsilon+2)^2 + \frac{M_2}{m_1} \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_s / \partial k} \right] \frac{1}{N\lambda^4 r^2}$$

### 3. *The Electron theory of Scattering by isotropic molecules.*

The problem of scattering of light can also be considered from a molecular standpoint. In this case the electromagnetic waves falling on a molecule produce a displacement of the electrons in that molecule. This is equivalent to creating an oscillating electric doublet in each molecule with a period the same as that of the waves. We shall however exclude the case of electrons having a natural period equal to the period of the incident waves. For isotropic molecules the axes of the doublets coincide in direction with that of the external electric force, but for anisotropic molecules the displacements of the electrons are not in general in that direction. The total effect may, however, be taken as equivalent to creating of three doublets with their axes along the three principal directions in each molecule. The field to which any molecule is subject is the resultant of that due to the incident wave and that due to the polarisation of the neighbouring molecules. In the following paragraphs, a method is developed from the molecular standpoint.

Consider a plane polarised wave travelling in the direction  $Ox$ . Let  $Z$  be the electric intensity in the wave parallel to  $Oz$  and proportional to  $\cos pt$ . Under the influence of the incident wave each molecule behaves as a doublet with its axis parallel to  $Oz$ . Let  $A_1$  be the moment induced in a molecule of the first component when it is placed in a field of unit intensity. Let  $A_2$  be the value for the second component of the mixture. Let  $n$  be the total number of molecules in a unit volume of the mixture of which  $n_1$  are of the first component and  $n_2$  of the second. Let  $M_1$  and  $M_2$  be the electrical moments of the doublets of the two components. The total intensity at any point in the medium is

$$Z + \frac{4\pi}{3} n_1 M_1 + \frac{4\pi}{3} n_2 M_2$$

and

$$\begin{aligned}
 M_1 &= A_1 \left( Z + \frac{4\pi}{3} n_1 M_1 + \frac{4\pi}{3} n_2 M_2 \right) \\
 &= \frac{A_1 Z}{1 - \frac{4\pi}{3} n_1 A_1} + \frac{A_1 \cdot \frac{4\pi}{3} n_2 M_2}{1 - \frac{4\pi}{3} n_1 A_1} \quad \dots \quad (12)
 \end{aligned}$$

Similarly

$$M_2 = \frac{A_2 Z}{1 - \frac{4\pi}{3} n_2 A_2} + \frac{A_2 \cdot \frac{4\pi}{3} n_1 M_1}{1 - \frac{4\pi}{3} n_2 A_2} \quad \dots \quad (12a)$$

The above equations can be written as

$$\begin{aligned}
 M_1 &= \frac{A_1 Z}{1 - \frac{4\pi}{3} n_1 A_1} + \frac{\frac{4\pi}{3} n_2 A_2 Z}{(1 - \frac{4\pi}{3} n_1 A_1)(1 - \frac{4\pi}{3} n_1 A_1 - \frac{4\pi}{3} n_2 A_2)} \\
 &= \frac{A_1 Z}{1 - \frac{4\pi}{3} n_1 A_1 - \frac{4\pi}{3} n_2 A_2} \quad \dots \quad (13)
 \end{aligned}$$

and similarly

$$M_2 = \frac{A_2 Z}{1 - \frac{4\pi}{3} n_1 A_1 - \frac{4\pi}{3} n_2 A_2} \quad \dots \quad (13a)$$

Now  $\epsilon_1$  the square of the refractive index of the first component for waves of frequency  $p/2\pi$  is given by

$$\frac{\epsilon_1 - 1}{\epsilon_1 + 2} = \frac{4\pi}{3} n'_1 A_1 \quad \dots \quad (14)$$

where  $n'_1$  is the number of molecules in a unit volume of the first component. For the second component we have similarly

$$\frac{\epsilon_2 - 1}{\epsilon_2 + 2} = \frac{4\pi}{3} n'_2 A_2 \quad \dots \quad (14a)$$

where  $n'_2$  is the number of molecules contained in a unit volume of the second component and  $\epsilon_2$  the square of the refractive index of the second component.

Remembering that

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\epsilon_1-1}{\epsilon_1+2} \cdot \frac{n_1}{n'_1} + \frac{\epsilon_2-1}{\epsilon_2+2} \cdot \frac{n_2}{n'_2}$$

where  $\epsilon$  is the square of the refractive index of the mixture the expressions for  $M_1$  and  $M_2$  become after some simplification

$$M_1 = A_1 Z \cdot \frac{\epsilon+2}{3} \quad \dots (15)$$

and

$$M_2 = A_2 Z \cdot \frac{\epsilon+2}{3} \quad \dots (15a)$$

A vibrating electric doublet radiates out energy. According to Hertz's well-known solution, the electric intensity at time  $t - \frac{r}{c}$  at a point  $r$  distant (great in comparison with  $\lambda$ ) from the doublet of moment  $M_1$ , is

$$\frac{p^2}{c^2 r} M_1 \Big|_{t-\frac{r}{c}} \sin \theta \quad \dots (16)$$

where  $c$  is the velocity of light in vacuo,  $\theta$  is the angle between  $Oz$  and the direction of the ray and  $M_1 \Big|_{t-\frac{r}{c}}$  stands for the value of the moment at time  $t - \frac{r}{c}$ .

For a medium containing molecules which are uniformly distributed, the effect due to a volume whose dimensions are large compared with  $\lambda$ , vanishes in all directions except in the direction of primary propagation where the secondary waves from the different molecules in the wave front combine with the original wave and give rise to a plane wave moving with an altered velocity. In any medium, containing a mixture of

liquids, however, owing to thermal movements of the molecules, and the consequent fluctuations of density and concentration at any point, there is a finite radiation of energy in all directions. If  $n$  represents the average number of molecules per unit volume in a volume element  $\delta v$  and  $\overline{\delta n^2}$  the mean square of the deviations of that number, then we have

$$\frac{\overline{\delta n^2}}{n_s} = \frac{RT\beta}{N\delta v} \quad \dots \quad (17)$$

If  $k$  is the concentration of the mixture, the mean square of the deviation of that quantity is given by

$$(\overline{\delta k})^2 = \frac{M_2}{\pi^2 N \delta v} \cdot \frac{1}{m_2 \partial \log p_2 / \partial k} \quad \dots \quad (18)$$

we have also the relation

$$(\overline{\delta k}) (\overline{\delta n}) = 0 \quad \dots \quad (19)$$

Consider a volume element  $\delta v$  small in comparison with the wave length, but large compared with the dimensions of a molecule. Let  $n$  be the average number of molecules present per unit volume in  $\delta v$  of which  $n_1$  are of the first component and  $n_2$  are of the second, so that  $n_1 + n_2 = n$ . If  $\rho$  is the density of the mixture, then  $n$  is proportional to  $\rho$ . To calculate the intensity of light scattered by the molecules in the volume  $\delta v$ , we have to take two factors into consideration—one is due to the variation of  $n$  or density  $\rho$  consequent on the variation of  $n_1$  and  $n_2$ , keeping the proportion of  $n_2$  to  $n_1$ , *i.e.*, the concentration  $k$  fixed. This part gives the scattering due to fluctuations of the density of the mixture taken as a single liquid. The other is due to the variation of the proportion of  $n_2$  to  $n_1$ , keeping the pressure constant. This part accounts for the scattering due to fluctuations in concentration.



The electric vector at P due to scattering by the molecules contained in a volume  $\delta v$  is given by

$$\begin{aligned} Z' &= \frac{p^2}{c^2 r} \sin \theta \delta v [(M_1 + \delta M_1)(n_1 + \delta n_1) - M_1 n_1 \\ &\quad + (M_2 + \delta M_2)(n_2 + \delta n_2) - M_2 n_2 + \frac{\partial}{\partial k} (M_1 n_1 + M_2 n_2) \delta k] \\ &= \frac{p^2}{c^2 r} \sin \theta \delta v [M_1 \delta n_1 + n_1 \delta M_1 + M_2 \delta n_2 + n_2 \delta M_2 \\ &\quad + \frac{\partial}{\partial k} (M_1 n_1 + M_2 n_2) \delta k] \end{aligned}$$

Since  $n_1 M_1 + n_2 M_2$ , is the total polarisation at the point O, it is proportional to  $(\epsilon - 1)/4\pi$  and hence

$$\frac{\partial}{\partial k} (n_1 M_1 + n_2 M_2) = \frac{Z}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k$$

The above expression therefore becomes

$$= \frac{p^2}{c^2 r} \sin \theta \delta v \left[ M_1 \delta n_1 + \delta M_1 n_1 + n_2 \delta M_2 + M_2 \delta n_2 + \frac{Z}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right] \quad \dots \quad (20)$$

To evaluate the expression  $M_1 \delta n_1 + n_1 \delta M_1 + M_2 \delta n_2 + n_2 \delta M_2$ , we have the relation—

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} (n_1 A_1 + n_2 A_2) \quad \dots \quad (21)$$

Now differentiating (21), we get after some simplification

$$\frac{4\pi}{3} (A_1 \delta n_1 + A_2 \delta n_2) = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{\delta n}{n} \quad \dots \quad (22)$$

From (15) and (21), we get in a similar manner

$$\begin{aligned} \delta M_1 &= A_1 Z \left( \frac{\epsilon + 2}{3} \right)^2 \left[ \frac{4\pi}{3} A_1 \delta n_1 + \frac{4\pi}{3} A_2 \delta n_2 \right] \\ &= A_1 Z \frac{(\epsilon - 1)(\epsilon + 2)}{9} \frac{\delta n}{n} \quad \dots \quad (23) \end{aligned}$$

Similarly

$$\delta M_2 = A_2 Z \frac{(\epsilon-1)(\epsilon+2)}{9} \frac{\delta n}{n} \quad \dots \quad (23a)$$

Substituting the values of  $\delta M_1$  and  $\delta M_2$  given by equations (23) and (23a) and taking the values of  $M_1$  and  $M_2$  given by relations (15) and (15a), we get with the help of equations (21) and (22).

$$M_1 \delta n_1 + n_1 \delta M_1 + n_2 \delta M_2 + M_2 \delta n_2 = Z \frac{(\epsilon-1)(\epsilon+2)}{12\pi} \frac{\delta n}{n} \quad \dots \quad (24)$$

Substituting the above value in equation (20), we get for the electric intensity at  $\rho$  due to scattering by the molecules contained in volume  $\delta v$

$$E = \frac{p^2 z}{c^2 r} \sin \theta \delta v \left[ \frac{(\epsilon-1)(\epsilon+2)}{12\pi} \frac{\delta n}{n} + \frac{1}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right] \quad \dots \quad (25)$$

The energy being proportional to  $E^2$  is given by

$$E^2 = \frac{p^4 Z^4}{c^4 r^2} \sin^2 \theta (\delta v)^2 \left[ \frac{(\epsilon-1)(\epsilon+2)}{12\pi} \frac{\delta n}{n} + \frac{1}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right]^2 \quad \dots \quad (26)$$

Since  $\delta n$  and  $\delta k$  vary from instant to instant according to the laws of chance the average expectancy of  $E^2$  over a sufficiently long interval of time is

$$E^2 = \frac{p^4 Z^4}{c^4 r^2} \sin^2 \theta \left[ \frac{(\epsilon-1)^2 (\epsilon+2)^2}{144\pi^2} \frac{\overline{\delta n^2}}{n^2} + \frac{1}{16\pi^2} \left( \frac{\partial \epsilon}{\partial k} \right)^2 \overline{(\delta k)^2} \right] (\delta v)^2$$

By (17) and (18), and remembering that  $p/c = 2\pi/\lambda$  we arrive at the formula (11. for a volume  $V$ .

#### 4. Scattering by anisotropic molecules.

When the arrangement of the electrons in a molecule is symmetrical, then the displacement of the electrons will be in the direction of the applied electric force and independent of

the direction. If it is unsymmetrical the displacement may not be in the direction of the force and scattered light will not be completely polarised. In this article the anisotropy of the molecules is taken into consideration in calculating the scattering of light by binary liquid mixtures.

Let  $O\xi_1, O\eta_1, O\zeta_1$ , denote the three principal directions in a molecule of the first component at right angles to each other such that the electrons can be displaced along any of them, without causing displacement along the other two. Similarly let  $O\xi_2, O\eta_2, O\zeta_2$ , denote the three principal directions of a molecule of the second component. Let  $Ox, Oy$ , and  $Oz$  be three fixed axes. Let  $A_1, B_1, C_1$ , be the moments induced in a molecule of the first component when placed in a field of unit intensity parallel to  $O\xi_1, O\eta_1, O\zeta_1$  respectively. Let  $A_2, B_2, C_2$  be the corresponding values for the second component. As before let  $Oz$  be the direction of the incident polarised plane wave and  $Z$  the electric intensity along  $Oz$ . The molecules being anisotropic, there will be components both along the  $x$  and  $y$  axes. But when the axes of the molecules are oriented at random the mean values of polarisation parallel to  $x$  and  $y$  axes vanish. But the value along the  $z$  axis which is

$$\frac{4\pi}{3}n_1 \overline{M_z} + \frac{4\pi}{3}n_2 \overline{M'_z},$$

is not zero, as  $M_z$  and  $M'_z$  which are the moments of each of the two components, can have only positive values.  $n_1$  and  $n_2$  are the number of molecules of the two components in unit volume.

The effect of polarisation of the surrounding molecules is then to produce an additional field of

$$\frac{4\pi}{3}n_1 \overline{M_z} + \frac{4\pi}{3}n_2 \overline{M'_z}.$$

The resultant electric field is therefore

$$Z + \frac{4\pi}{3}n_1 \overline{M_z} + \frac{4\pi}{3}n_2 \overline{M'_z},$$

To calculate  $\bar{M}_z$  we note that if the molecules are oriented at random

$$\begin{aligned}\bar{M}_z &= \frac{A_1 + B_1 + C_1}{3} \left[ Z + \frac{4\pi}{3} n_1 \bar{M}_z + \frac{4\pi}{3} n_2 \bar{M}'_z \right] \\ &= \frac{A_1 + B_1 + C_1}{3} \frac{\epsilon + 2}{3} Z \quad \dots \quad (27)\end{aligned}$$

as in the previous section.

$$M'_z = \frac{A_2 + B_2 + C_2}{3} \frac{\epsilon + 2}{3} Z \quad \dots \quad (27a)$$

and

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \left[ \frac{A_1 + B_1 + C_1}{3} n_1 + \frac{A_2 + B_2 + C_2}{3} n_2 \right] \quad \dots \quad (28)$$

If  $\theta, \phi, \psi$  are the Eulerian co-ordinates defining a molecule of the first component with respect to the fixed axes, we have for the moments induced in the molecule parallel to  $O\xi_1, O\eta_1, O\zeta_1$ ,

$$-A_1 Z \frac{\epsilon + 2}{3} \sin \theta \cos \phi, \quad B_1 Z \frac{\epsilon + 2}{3} \sin \theta \sin \phi, \quad C_1 Z \frac{\epsilon + 2}{3} \cos \theta \quad \dots \quad (29)$$

When these are resolved along  $Ox, Oy, Oz$  the components are

$$\begin{aligned}M_x &= Z \cdot \frac{\epsilon + 2}{3} [\sin \theta \cos \theta \cos \psi (C_1 - A_1 \cos^2 \phi - B_1 \sin^2 \phi) \\ &\quad + (A_1 - B_1) \sin \theta \sin \psi \sin \phi \cos \phi] \quad \dots \quad (30)\end{aligned}$$

$$\begin{aligned}M_y &= Z \cdot \frac{\epsilon + 2}{3} [\sin \theta \cos \theta \sin \psi (C_1 - A_1 \cos^2 \phi - B_1 \sin^2 \phi) \\ &\quad + (A_1 - B_1) \sin \theta \cos \psi \sin \phi \cos \phi] \quad \dots \quad (31)\end{aligned}$$

$$M_z = Z \cdot \frac{\epsilon + 2}{3} [C_1 \cos^2 \theta + B_1 \sin^2 \theta \sin^2 \phi + A_1 \sin^2 \theta \cos^2 \phi] \quad \dots \quad (32)$$

which for shortness, we may write

$$Z \cdot \frac{\epsilon+2}{3} \mathcal{L}_1, \quad Z \cdot \frac{\epsilon+2}{3} \mathcal{L}_2, \quad Z \cdot \frac{\epsilon+2}{3} \mathcal{L}_3$$

Similarly if  $\theta', \phi', \psi'$  are the values of  $\theta, \phi$  and  $\psi$  for the second component, we get

$$M'_x = Z \cdot \frac{\epsilon+2}{3} \mathcal{L}'_1, \quad \dots \quad (30a)$$

$$M'_y = Z \cdot \frac{\epsilon+2}{3} \mathcal{L}'_2, \quad \dots \quad (31a)$$

$$M'_z = Z \cdot \frac{\epsilon+2}{3} \mathcal{L}'_3, \quad \dots \quad (32a)$$

where  $\mathcal{L}'_1, \mathcal{L}'_2$ , and  $\mathcal{L}'_3$  are the expressions for  $\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3$  with  $\theta', \phi'$  and  $\psi'$ , written for  $\theta, \phi$  and  $\psi$  respectively and  $A_2, B_2, C_2$  written for  $A_1, B_1, C_1$  respectively.

To calculate the intensity of light scattered in any direction from a unit volume, we have to add together the contributions from all the molecules contained in it, due regard being paid to the phases of the waves scattered. In the case of isotropic molecules the induced moments are all parallel to the external field and the direction of vibration in the scattered light is parallel to that in the incident. With anisotropic molecules, however, the scattered light has also in general, vibrations perpendicular to those in the incident. In a binary liquid mixture containing isotropic molecules, the scattering can be supposed to arise from density and concentration fluctuations and in a medium containing anisotropic molecules, we have in addition scattering due to random character of the orientations of the molecules. In calculating the intensity of light scattered by a mixture of anisotropic molecules, we may suppose them to be replaced by isotropic molecules, having the same induced moments as the

average moment of the anisotropic molecules and proceed to calculate the intensity of scattered light due to fluctuations of density and concentration as in the previous section.

Thus in the case of a unit volume of the mixture containing  $n_1$  molecules of the first component and  $n_2$  of the second the sum of the induced moments in the direction of the  $x$ -axis is given by

$$\frac{4\pi}{3} (n_1 \bar{M}_x + n_2 \bar{M}'_x)$$

where  $\bar{M}_x$  and  $\bar{M}'_x$  are the mean values for the  $x$ -component of the moments of the two kinds of molecules. From (30) and (30a), the mean values will be zero. Similarly the  $y$ -component is zero and the  $z$ -component is given by

$$\frac{4\pi}{3} (\bar{M}_z n_1 + \bar{M}'_z n_2),$$

*i.e.*,

$$\frac{4\pi}{3} \frac{\epsilon+2}{9} [(\Lambda_1 + B_1 + C_1)n_1 + (\Lambda_2 + B_2 + C_2)n_2]$$

We can now proceed exactly as in the case of isotropic molecules, to find the intensity of light scattered by a unit volume of the mixture due to density and concentration fluctuations, for which we get similar expressions as in the previous section.

Actually, however, each anisotropic molecule has in any direction a moment different from the average value on account of its varying orientation, and the fluctuation of the value of the moment from its mean value gives rise to an additional scattering. Thus for a unit volume, the fluctuations in moments from their average values in the direction are given by

$$M_x n_1 + M'_x n_2, \quad M_y n_1 + M'_y n_2$$

and

$$\frac{\epsilon+2}{3} \left[ \left( \frac{\Lambda_1 + B_1 + C_1}{3} - \underline{L}_3 \right) n_1 + \left( \frac{\Lambda_2 + B_2 + C_2}{3} - \underline{L}'_3 \right) n_2 \right]$$

We shall now proceed to calculate the light scattered by a unit volume of the mixture arising out of the two ways mentioned above.

At a point on the  $y$ -axis distant  $r$  from O, the  $x$ -component of the electric vector due to scattering from a molecule at O is

$$\frac{p^2}{c^2 r} M_x$$

The total effect of all the molecules contained in a small volume element  $\delta v$ , which is small compared with the wavelength but large compared with the linear dimensions of the molecule is given by

$$X' = \frac{p^2}{c^2 r} \sum M_x$$

Since  $\delta v$  contains a large number of molecules with their orientations at random  $\sum M_x$  would in general be small, as positive and negative values of  $M_x$  are equally probable. Indeed when the number of molecules is large the mean value would be zero. But the value of  $(\sum M_x)^2$  however when  $M_x$  is as often positive as negative is, as the late Lord Rayleigh<sup>1</sup> has shown,

$$(\overline{\sum M_x})^2 = n \cdot \overline{M_x^2} \delta v \quad \dots (33)$$

where  $n\delta v$  is the number of molecules in  $\delta v$ . For a binary mixture containing  $n_1\delta v$  and  $n_2\delta v$  molecules of the two components the average expectation  $X'^2$  is

$$X'^2 = \frac{p^4}{c^4 r^2} (\overline{M_x^2} n_1 + \overline{M_x'^2} n_2) \delta v$$

<sup>1</sup> Theory of Sound, Vol. 1, Art. 42a.

Substituting the values of  $M_x$  and  $M'_x$  given by (30) and (30a) and averaging over all orientations of the molecules

$$\begin{aligned}\bar{X}^2 &= \frac{P^2 Z^2}{c^2 r^2} \left( \frac{\epsilon+2}{3} \right)^2 \cdot \frac{1}{15} [(A_1^2 + B_1^2 + C_1^2 - A_1 B_1 - B_1 C_1 - C_1 A_1) n_1 \\ &\quad + (A_2^2 + B_2^2 + C_2^2 - A_2 B_2 - B_2 C_2 - C_2 A_2) n_2] \delta v \quad \dots (34) \\ &= \frac{P^2 Z^2}{c^2 r^2} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2)\end{aligned}$$

where

$$f_1 = \frac{1}{15} (A_1^2 + B_1^2 + C_1^2 - A_1 B_1 - B_1 C_1 - C_1 A_1)$$

and

$$f_2 = \frac{1}{15} (A_2^2 + B_2^2 + C_2^2 - A_2 B_2 - B_2 C_2 - C_2 A_2)$$

For a volume  $V$ ,

$$\bar{X}^2 = \frac{P^2 Z^2}{c^2 r^2} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) V \quad \dots (35)$$

In the case of the  $z$ -component of the electric intensity at  $P$  in the waves scattered from a volume element  $\delta v$ , we have, as seen above, to take into consideration two parts—one, the scattering due to the molecules, when they are replaced by isotropic molecules having the same average moment as the anisotropic molecules. This gives, as in the previous section, scattering due to density and concentration fluctuations. The other is due to fluctuation of the moments of the anisotropic molecules on account of their varying orientations. The second part as in the case of the  $x$ -component of the electric intensity is proportional to the number of molecules and the first is proportional to the square of that number.



The first part of the square of the  $z$ -component of the electric vector at P in the waves scattered from a volume  $\delta v$  at O, is given as in the case of isotropic molecules, by

$$\begin{aligned}
 & P^4 Z^2 (\delta v)^2 \cdot \left\{ \left[ \delta(M_1 n_1 + M'_1 n_1) \right]^2 + \left[ \frac{\partial}{\partial k} (M_1 n_1 + M'_1 n_1) \delta k \right]^2 \right\} \\
 &= \frac{P^4 Z^2}{c^4 r^2} (\delta v)^2 \left[ \left( \frac{\epsilon+2}{3} \right)^4 (M_1 \delta n_1 + M'_1 \delta n_1)^2 + \left( \frac{1}{4\pi} \frac{\partial \epsilon}{\partial k} \delta k \right)^2 \right] \\
 &= \frac{P^4 Z^2}{c^4 r^2} (\delta v)^2 \left[ \frac{(\epsilon-1)^2 (\epsilon+2)^2}{144\pi^2} \frac{\delta n^2}{n^2} + \frac{1}{16\pi^2} \left( \frac{\partial \epsilon}{\partial k} \delta k \right)^2 \right] \quad \dots (36)
 \end{aligned}$$

The second part for a volume  $\delta v$  is given by

$$\begin{aligned}
 & \frac{P^4 Z^2}{c^4 r^2} \left( \frac{\epsilon+2}{3} \right)^2 \left\{ \left( \underline{A}_1 + \underline{B}_1 + \underline{C}_1 - \underline{L}_1 \right) n_1 \right. \\
 & \quad \left. + \left( \underline{A}_2 + \underline{B}_2 + \underline{C}_2 - \underline{L}_2 \right) n_2 \right\} \delta v
 \end{aligned}$$

This reduces for all orientations to

$$\frac{P^4 Z^2}{c^4 r^2} \left( \frac{\epsilon+2}{3} \right)^2 \frac{4}{3} (f_1 n_1 + f_2 n_2) \delta v \quad \dots (37)$$

Hence the total value of the square of the  $z$ -component of the electric vector is given by

$$\begin{aligned}
 \overline{Z^2} &= \frac{1}{c^4 r^2} \left[ \left\{ \frac{(\epsilon-1)^2 (\epsilon+2)^2}{144\pi^2} \frac{\overline{\delta n^2}}{n^2} + \frac{1}{16\pi^2} \left( \frac{\partial \epsilon}{\partial k} \right)^2 (\overline{\delta k})^2 \right\} (\delta v)^2 \right. \\
 & \quad \left. + \frac{4}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) \delta v \right] \quad \dots (38)
 \end{aligned}$$

Substituting the values of  $(\delta n)^2$  and  $(\delta k)^2$  from (26) and (27) we get

$$\begin{aligned} \overline{Z}^2 = \frac{P^4 Z^4}{c^4 r^4} \left[ \left\{ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{\frac{M_2}{m_1} (\partial \epsilon / \partial k)^2}{N \partial \log p_2 / \partial k} \right\} \right. \\ \left. + \frac{4}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) \right] \delta v \end{aligned}$$

For a volume V,

$$\begin{aligned} \overline{Z}^2 = \frac{P^4 Z^4}{c^4 r^4} \left[ \left\{ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{\frac{M_2}{m_1} (\partial \epsilon / \partial k)^2}{N \partial \log p_2 / \partial k} \right\} \right. \\ \left. + \frac{4}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) \right] V. \quad \dots (39) \end{aligned}$$

When the incident light is unpolarised the ratio of the two components is given by

$$\begin{aligned} \gamma = \frac{2 \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2)}{\frac{7}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) + \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2 (\partial \epsilon / \partial k)^2}{N m_1 \partial \log p_2 / \partial k}} \quad \dots (40) \end{aligned}$$

The total intensity of the scattered light for a volume V is given by

$$\begin{aligned} \frac{P^4 Z^4}{c^4 r^4} V \left\{ \frac{13}{3} \left( \frac{\epsilon+2}{3} \right)^2 (f_1 n_1 + f_2 n_2) + \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} \right. \\ \left. + \frac{1}{16\pi^2} \cdot \frac{M_2 (\partial \epsilon / \partial k)^2}{N m_1 \partial \log p_2 / \partial k} \right\} \\ = \frac{P^4 Z^4}{c^4 r^4} V \left\{ \frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \cdot \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_2 (\partial \epsilon / \partial k)^2}{N m_1 \partial \log p_2 / \partial k} \right\} \end{aligned}$$

$$\left[ 1 + \frac{\frac{13}{3} \cdot (f_1 n_1 + f_2 n_2)}{\frac{(\epsilon-1)^2(\epsilon+2)^2}{144\pi^2} \frac{RT\beta}{N} + \frac{1}{16\pi^2} \cdot \frac{M_1 (\partial \epsilon / \partial k)^2}{N m_1 \partial \log p_s / \partial k}} \right]$$

This reduces after a little simplification to

$$\frac{V}{r^2} \cdot \left\{ \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (\epsilon-1)^2(\epsilon+2)^2 + \frac{M_1 (\partial \epsilon / \partial k)^2}{N\lambda^4 m_1 \partial \log p_s / \partial k} \right\} \left[ \frac{6(1+\gamma)}{6-7\gamma} \right] \quad \dots (41)$$

where  $\lambda$  is the wave-length in vacuo. The above formula can be seen to be the same expression as for the isotropic molecules multiplied by the Cabannes' factor.

In the case of a single substance the above reduces to

$$\frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (\epsilon-1)^2(\epsilon+2)^2 \cdot \frac{6(1+\gamma)}{6-7\gamma} \quad \dots (41a)$$

### PART III.

#### *Comparison of Theory and Experiment.*

##### 1. INTENSITY.

The intensity of light scattered by mixtures of toluene and acetic acid at the room temperature will be considered. Toluene is taken as the first component and acetic acid as the second. In calculating the density and concentration scatterings the common multiplying factor  $1/N\lambda^4$  is omitted. The compressibility data are taken from Cohen and Schut's *Piezo Chemie*. The compressibilities for different concentrations are given in the following table.

TABLE VII.

Liquid.	Toluene	K=0.197	K=0.575	K=1.651	K=3.03	Acetic acid
$\beta \cdot 10^6$	91.4	82	87	85	89	96

The variation of refractive index with concentration is calculated for the F-line from the following well-known formula

$$\frac{\epsilon-1}{\epsilon+2} \cdot \frac{1}{\rho} = \frac{\epsilon_1-1}{\epsilon_1+2} \cdot \frac{f_1}{\rho_1} + \frac{\epsilon_2-1}{\epsilon_2+2} \cdot \frac{f_2}{\rho_2} \quad \dots (42)$$

where  $\epsilon$ ,  $\epsilon_1$ ,  $\epsilon_2$  are respectively the refractive indices of the mixture and the two components,  $\rho$ ,  $\rho_1$ ,  $\rho_2$  are respectively the densities of the mixtures and the two components,  $f_1$  and  $f_2$  are the fractions of the masses of each of the two components in the total mass of the mixture. The values of  $\epsilon$  for different concentrations are given in the table VIII.

TABLE VIII.

K	Toluene	0.11	0.25	0.43	0.67	1.0	1.25	2.33	4.0	9.0	Acetic acid
$\epsilon$	2.281	2.247	2.210	2.172	2.135	2.096	2.058	2.018	1.978	1.936	1.894

Though the incident light is not homogeneous, as we are concerned only with the ratios and not with the absolute values, we will not be far from right if we take the refractive indices corresponding to the F line as representative of the whole. From Tables VII and VIII the compressibilities and refractive indices for the required concentrations are obtained by interpolation. Knowing  $R$  to be equal to  $83.15 \times 10^6$  C.G.S. units, the values of  $\Omega_1$ ,  $N\lambda^4$  are calculated. where

$$\Omega_1 = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} \cdot (\epsilon-1)^2(\epsilon+2)^2.$$

For calculating the concentration scattering, the variation of  $\log p_2$  where  $p_2$  is the partial vapour pressure of the second component (acetic acid in this case), with concentration is given in the following table :

TABLE IX.

K	0	0.03	0.069	0.135	0.206	0.318	0.451	0.567	0.690	0.971	1.437	2.171	4.565	Acetic acid
$\log p_2 - 2$	0	0.542	1.115	1.537	1.754	1.936	2.057	2.125	2.177	2.259	2.332	2.405	2.489	2.610

The variation of  $\epsilon$  with  $k$  is given in the Table VIII. The values of  $\delta \log p_2 / \partial k$  are found by the usual method after drawing a graph with  $k$  as abscissa and  $\log p_2$  as ordinate. In a similar manner,  $\partial \epsilon / \partial k$  is found from another graph. Then the values of  $\Omega_2$ ,  $N\lambda^1$  are calculated,

$$\text{where} \quad \Omega_2 = \frac{M_2}{2N\lambda^2 m_1} \left[ \frac{(\partial \epsilon / \partial k)^2}{\partial \log p_2 / \partial k} \right]$$

The orientation scattering is first calculated for toluene and acetic acid from equation (4) of paper A after knowing the ratio of the two components of polarisation from the observed values. From (35) the orientation scattering for any mixture divided by  $\left(\frac{\epsilon+1}{3}\right)^2$  is proportional to the number of molecules of each component, the variations of  $4\Omega_2 / \left(\frac{\epsilon+2}{3}\right)^2$  with  $k$  will be linear and the orientation scattering is easily calculated. The following table gives the calculated and observed intensities for the transversely scattered light :

TABLE X.

Liquid	Percentage Volume of CS <sub>2</sub>	Concentration K	$\Omega_1 N\lambda^2$	$\Omega_2 N\lambda^2$	$4\Omega_2 N\lambda^2$	TOTAL		TOTAL SCATTERING / TOLUENE SCATTERING		
						$(\Omega_1 + \Omega_2 + 4\Omega_2) / N\lambda^2$	According to (41)	Calculated R & R <sup>1</sup>	J.C.K. <sup>2</sup>	Observed.
Toluene	100		37.2	0	91	128	143.5	1.0	1.0	1.0
A	83.3	0.24	28.9	20	82	131	157	1.03	1.11	1.05
B	66.7	0.61	26.8	30	73	130	141	1.04	1.0	1.0
C	50.0	1.21	22.7	38	65	126	135	1.0	0.91	1.0
D	33.3	2.43	19.5	34.6	58	103	114	0.81	0.8	0.78
E	16.7	6.07	17.7	14.9	51	84	90	0.65	0.63	0.70
Acetic acid	0		15.7	0	44	60	78.4	0.47	0.55	0.5

<sup>1</sup> R & R Raman and Ramanathan's formula corrected for orientation scattering.

<sup>2</sup> J. C. K. Formula given by equation (41).

A graph fig. 1 with the percentage volume of toluene as abscissa and the intensity as ordinate is given. The dotted curve shows the observed values and the other one shows the calculated values, from formula (41).

In the above table X and fig. 1 one sees a fairly good agreement between the calculated and observed values.

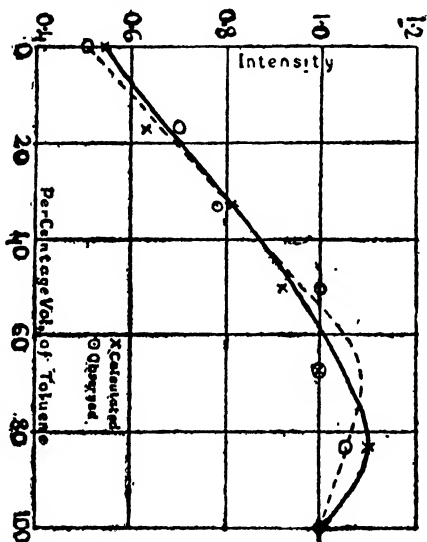


Fig. 1.

We shall now consider the intensity of scattered light by mixtures of methyl alcohol and carbon bisulphide at different temperatures. In the calculations carbon bisulphide is taken as the second component and methyl alcohol as the first. In calculating the density and concentration scattering the common multiplying factor  $1/N\lambda^4$  is omitted as in the previous case. Experimental data for the compressibilities of the mixture are not available. The variation of compressibility with concentration is assumed to be similar to the mixtures of carbon bisulphide and methyl alcohol (for which data is available), the relation being almost linear. The necessary correction for variation with temperature is also made.

The variation of refractive index with concentration is calculated as before for the F line and for calculating

variations with temperature Lorentz's formula is employed. The following table gives the squares of the refractive indices for different concentrations and temperatures.

TABLE XI.  
SQUARES OF REFRACTIVE INDICES

Temp.	CH <sub>3</sub> OH	K=0.12	K=0.25	K=0.43	K=0.67	K=1.0	K=1.5	K=2.33	K=4.0	K=9.0	CS <sub>2</sub>
20	1.777	1.827	1.884	1.943	2.016	2.095	...	...	...	...	2.732
30	1.769	1.814	1.872	1.929	1.995	2.077	...	...	...	2.529	2.699
40	1.754	1.802	1.866	1.914	1.983	2.060	2.155	2.249	2.304	2.502	2.670
50	1.744	1.791	1.858	1.901	1.968	2.041	2.138	2.229	2.344	2.478	2.640
60	1.733	1.778	1.840	1.887	1.952	2.028	2.120	2.208	2.320	2.453	2.611

The compressibilities and the squares of the refractive indices for different concentrations and temperatures being known, and knowing  $R$  to be equal to  $83.15 \times 10^8$  C. G. S. units, the values of  $\Omega_1 \cdot N\lambda^4$  are calculated. The values of  $\partial \epsilon / \partial k$  for different temperatures and concentrations are obtained as in the previous case. There now remains the factor  $\partial \log p_2 / \partial k$  to calculate the concentration scattering. In the absence of experimental data recourse had to be taken to theoretical methods of calculation. The total vapour pressures for different concentrations and temperatures are first determined by the usual method. For temperatures above the critical solution temperature Porter's method<sup>1</sup> was applied by using the formula.

$$P = \Pi_a \mu_a e^{\beta(1-\mu_a)^2} + \Pi_b \mu_b e^{\beta\mu_a^2} \quad \dots (43)$$

where  $P$  is the total vapour pressure,  $\Pi_a$  and  $\Pi_b$  are the vapour pressures of the two constituents at the same temperature,  $\mu_a$  and  $\mu_b$  are the molecular fractions of the two constituents, and  $\beta$  is a constant slightly decreasing with increasing temperatures. All the quantities in the above equation except  $\beta$  are known. After getting a proper value of  $\beta$ , the partial vapour pressures are calculated from the

<sup>1</sup> Trans. Farad. Soc., Vol. XVI, p. 336,

formula

$$\pi_a = \Pi_a \mu_a e^{\beta(1-\mu_a)^2}$$

where  $\pi_a$  is the partial pressure corresponding to the molar fraction  $\mu_a$ . This approximate but very useful formula, which fitted in well for temperatures above the critical temperature, failed to give concordant results for lower temperatures. For these temperatures, Marshall's graphical method<sup>1</sup> which is also based on the general solution of Duhem's equation was used. This method though very tedious, was found to give more concordant results. The above methods of calculating partial vapour pressures are also justified by the fact, that when they are applied to cases where experimental data are available, the calculated values agreed very well with the experimental values. The results of these calculations for mixtures of methyl alcohol and carbon bisulphide are given in the following fig. 2.

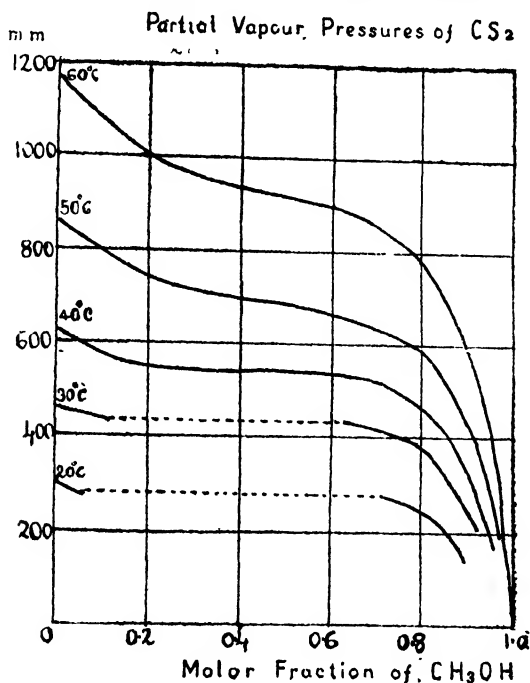


Fig. 2.

<sup>1</sup> Trans. Chem. Soc., Vol. 89, p. 1350.



The molar fractions of methyl alcohol are given as abscissa and the partial vapour pressure of carbon bisulphide as ordinate. It is easily seen from the curve corresponding to the critical solution temperature, that there is a point of inflection. For curves corresponding to lower temperatures there are two concentrations corresponding to the two layers for which the partial pressure is the same. To get the values of  $\partial \log p_2 / \partial k$ , the above graphs are redrawn with  $k$  as abscissa and  $\log p_2$  as ordinates and from these graphs the values of  $\partial \log p_2 / \partial k$  are calculated. Thus all factors being known,  $\Omega_s \cdot N\lambda^4$  is easily calculated.

The orientation scattering for any temperature for methyl alcohol and carbon bisulphide is calculated from (41a) as in the previous case. From these, the values for other concentrations are easily calculated from (35).

The following tables give the calculated and observed intensities for the transversely scattered light, for different temperatures and different concentrations.

TABLE XII (a).

 $t = 20^\circ\text{C}$ 

Liquid	Percentage Volume of $\text{CS}_2$	Concentration $K = m_2/m_1$	$\Omega_1 \cdot N\lambda^4$	$\Omega_2 \cdot N\lambda^4$	$4\Omega_3 \cdot N\lambda^4$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						J.C.K.	R&R	Calculated		Observed
								R&R	J.C.K.	
$\text{CH}_3\text{OH}$	0	...	14	0	1	17	15	0.05	0.06	0.08
A	25	0.5	21	96	65	183	182	0.6	0.60	0.72
B	40	1.0	28	1264	110	1573	1402	5.0	5.1	5.0
$\text{CS}_2$	100	.	77	0	359	714	436	1.5	2.5	1.5

TABLE XII (b).

 $t = 30^{\circ}\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\alpha_1 \cdot N\lambda^*$	$\alpha_2 \cdot N\lambda^*$	$4\alpha_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						R&R	J.C.K.	Calculated		Observed
								R&R	J.C.K.	
$\text{CH}_3\text{OH}$	0	.	15	0	1.5	16.5	18	0.06	0.06	0.08
A	25	0.5	22	96	69	187	185	0.6	0.6	0.74
B	48	1.4	30	1467	47	1644	1706	5.9	6.0	6.5
$\text{CS}_2$	100	...	82.6	0	386	469	765	1.7	2.6	1.6

TABLE XII (c).

 $t = 40.5^{\circ}\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\alpha_1 \cdot N\lambda^*$	$\alpha_2 \cdot N\lambda^*$	$4\alpha_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						R&R	J.C.K.	Calculated		Observed
								R&R	J.C.K.	
$\text{CH}_3\text{CH}$	0	.	16	0	2	18	20	0.06	0.07	.1
A	25	0.5	23	157	72	251	242	0.9	0.85	.90
B	50	1.6	38	5350	166	5554	6008	20	21	23
C	75	5.0	16.7	$\infty$	270	inf	inf	inf.	inf.	80
$\text{CS}_2$	100	.	87	0	407	494	807	1.75	2.6	1.75

TABLE XII (d).

 $t = 50^{\circ}\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\alpha_1 \cdot N\lambda^*$	$\alpha_2 \cdot N\lambda^*$	$4\alpha_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						R&R	J.C.K.	Calculated		Observed
								R&R	J.C.K.	
$\text{CH}_3\text{OH}$	0	...	17.2	0	2	19	21.5	0.07	0.07	0.1
A	25	0.5	25.2	142	76	243	277	0.9	1.0	1
B	50	1.6	40.6	2246	171	2458	2663	8.4	9.0	14.5
C	75	5.0	65.6	5432	284	5782	6077	20	21	16
$\text{CS}_2$	100	...	91.6	0	427	519	853	1.8	2.9	1.7

TABLE XII (e).

 $t = 60^\circ\text{C}$ 

Liquid	Percentage Vol. of $\text{CS}_2$	K	$\Omega_1 \cdot N\lambda^*$	$\Omega_2 \cdot N\lambda^*$	$4\Omega_3 \cdot N\lambda^*$	TOTAL		TOTAL SCATTERING/ TOLUENE SCATTERING		
						Calculated		Calculated		Observed
						R&R	J.C.K.	R&R	J.C.K.	
$\text{CH}_3\text{OH}$	0	.	18.4	0	2	20.4	22.4	0.07	0.08	0.1
A	25	0.5	26.7	200	81	308	381.6	1.0	1.31	1.33
B	50	1.6	43	1180	180	1403	1523	5.0	5.3	6
C	75	5.0	69	1766	283	2118	2285	7.3	8.0	9
$\text{CS}_2$	100	..	96	0	440	545	890	1.9	3.1	2

Three typical graphs corresponding to tables XIIb, XIIc and XIId are drawn. The percentage volume of carbon bisulphide is given as abscissa and the intensity as ordinate. The dotted lines in all cases denote the observed values.

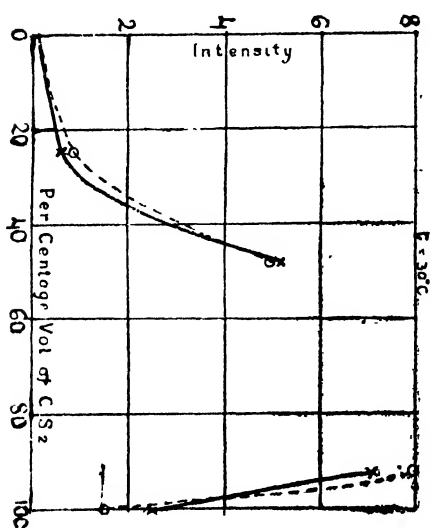


Fig. 3.

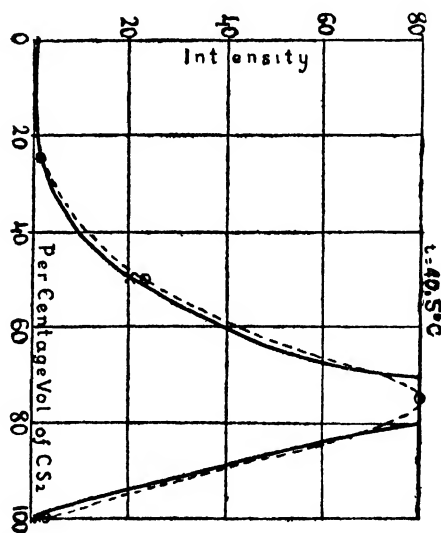


Fig. 4.

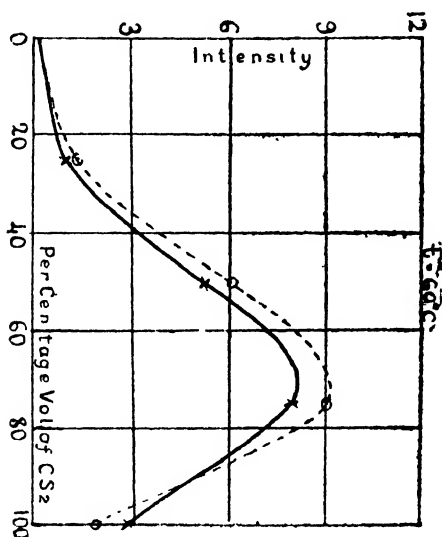


Fig. 5.

## 2. POLARISATION.

Knowing the values of  $\gamma$  for Toluene and acetic acid, obtained by direct observation, the values of  $\gamma$  for the mixtures are calculated from (41a) neglecting  $\alpha_1$ . The calculated and observed values are given in the following table for comparison :

TABLE XIII.

Liquid	Percentage Vol. of Toluene.	K	100 $\gamma$	
			Calculated.	Observed.
Toluene	100	.	55	55
A	83.3	.24	51	46.5
B	66.7	.61	39	37.8
C	50	1.21	35	33.8
D	33.3	2.43	35	32.5
E	16.7	6.07	44	45.6
Acetic Acid	0	..	58.5	58.5

A graph Fig. 6 with percentage volume of toluene as abscissa and  $100\gamma$  as ordinate is also given.

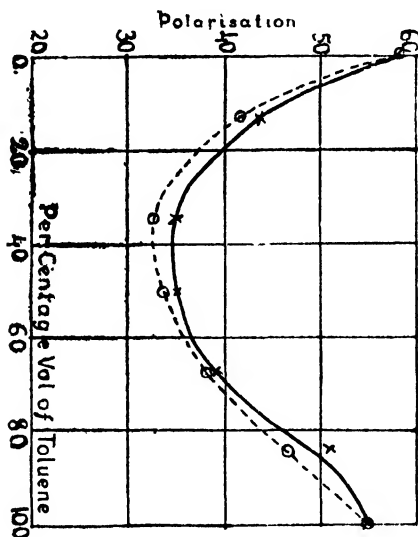


Fig. 6.

In a similar way, knowing the values of  $\gamma$  for methyl alcohol and carbon bisulphide obtained by direct observation, the values of  $100\gamma$  for the mixtures are calculated as before. The calculated and observed values for different temperatures and concentrations are given in the following tables.

TABLE XIV (a).

 $t = 20^\circ\text{C}$ 

Liquid.	Percentage Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated	Observed
$\text{CH}_3\text{OH}$	0	...	9	9
A	25	0.5	22	30.3
B	40	1.0	4.1	9
$\text{CS}_2$	100	...	70	70

TABLE XIV (b).

 $t = 30^{\circ}\text{C}$ 

Liquid	Percent. Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated.	Observed.
$\text{CH}_3\text{OH}$	0	.	9	9
A	25	0.5	22	20
B	48	1.4	4.7	6
$\text{CS}_2$	100	...	70	70

TABLE XIV (c).

 $t = 40.5^{\circ}\text{C}$ 

Liquid	Percent. Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated.	Observed.
$\text{CH}_3\text{OH}$	0	..	9	9
A	25	0.5	16.7	16.3
B	50	1.6	1.5	5.1
C	75	5.0	0	3.0
$\text{CS}_2$	100	...	70	70

TABLE XIV (d).

 $t = 50^{\circ}\text{C}$ 

Liquid	Percent. Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated.	Observed.
$\text{CH}_3\text{OH}$	0	.	9	9
A	25	0.5	18.5	22.5
B	50	1.6	3.6	7
C	75	5.0	2.5	4.6
$\text{CS}_2$	100	.	69	96

TABLE XIV(e).

 $t=60^{\circ}\text{C}$ 

Liquid	Percent. Vol. of $\text{CS}_2$	K	100 $\gamma$	
			Calculated.	Observed.
$\text{OH}_3\text{OH}$	0	...	9	9
A	25	0.5	15	23
B	50	1.6	7	10
C	75	0.5	7	10
$\text{CS}_2$	100	...	69	69

Two typical graphs corresponding to Tables XIVc and XIVe are given in figures (7) and (8). The percentage volumes of  $\text{CS}_2$  are given as abscissa and 100 $\gamma$  as the ordinate. The tables and figures show also a fair agreement between theory and experiment.

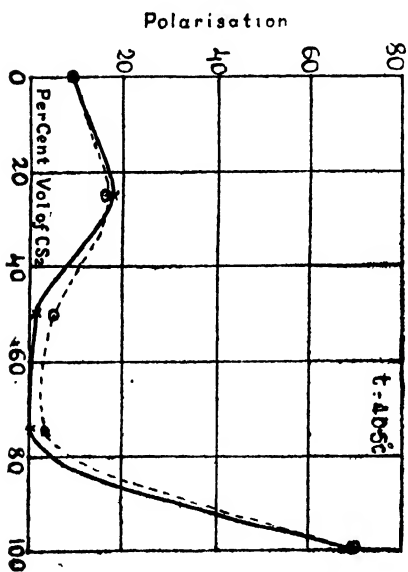


Fig. 7.

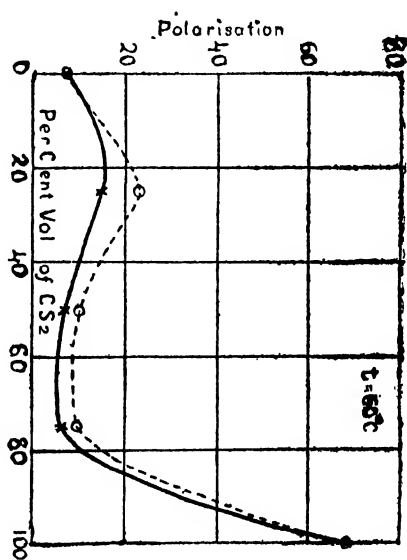


Fig. 8.

## PART IV.

*Summary and Conclusion.*

The paper describes experimental and theoretical work dealing with the scattering of light by binary liquid mixtures. Part I deals with the experimental work done on measurement of the intensity of light scattered by mixtures of toluene and acetic acid at the room temperature and by mixtures of methyl alcohol and carbon bisulphide at different temperatures. It gives also the state of polarisation of the scattered light for the same pairs of liquids. The variation of the intensity of light scattered by the second pair of liquids is very interesting and instructive. The intensity at any temperature increases with concentration till a particular concentration is reached beyond which it again decreases. This effect is very great at the critical temperature while for the critical concentration, the intensity is enormous, but above and below this, it decreases. The state of polarisation shows also similar interesting changes. For any temperature, the imperfectness of polarisation is a minimum for a particular concentration; this effect being more prominent at the critical temperature: at which the scattered light is almost completely polarised for the critical concentration, the light becomes more and more imperfectly polarised at higher or lower temperatures.

Part II, art. 2, discusses an electromagnetic theory of the scattering of light in binary liquid mixtures without assuming a molecular structure, on the basis of Lorentz's treatment of the scattering of light in gases. By this method Raman and Ramanathan's formula is derived. The same result is shown to follow if the medium is endowed with a molecular structure and the molecules are assumed to be isotropic. The same treatment is extended to the case of anisotropic molecules,



in which case it is shown that if the molecules are entirely oriented at random, the transversely scattered light is imperfectly polarised. The intensity of the light scattered in a direction at right angles to the primary beam is shown to be

$$\frac{V}{r^2} \left[ \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (\epsilon-1)^2 (\epsilon+2)^2 + \frac{M_2 (\partial \epsilon / \partial k)^2}{N\lambda^4 \cdot m_1 \partial \log p_2 / \partial k} \right] \frac{6(1+r)}{6-7r} .$$

Part III gives the comparison of the results obtained by theory and experiment and shows a fair agreement between the two.

In conclusion, the author wishes to express his best thanks to Prof. C. V. Raman who suggested the problem, for his helpful interest and encouragement.

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# On the Modification of the Laws of Emission of Ions from Hot Metals by the Quantum Theory<sup>1</sup>

By

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1. *Introduction.*—Although the classical electron theories of metals, developed by Drude, Lorentz, Thomson and others, have given us a fair account of the various outstanding physical properties of metals,—such as the heat and electrical conductivity, the Peltier-effect, the Thomson-effect, the Richardson-effect and so on, the various secondary hypotheses which have been advanced to explain these phenomena are seldom convincing and are often in absolute contradiction with one another. The most obvious difficulty, however, is the question of the heat-capacity of metals. If the ‘free’ conduction electrons could claim their full share in the equal distribution of kinetic energy, then this share of energy should be plainly noticeable in the atomic heats of these bodies. Such an increase in the atomic heats of metals as compared to metalloids which contain vanishingly few free electrons, has never been discovered. Further, as Lorentz has pointed out, the classical electron theory invariably leads to Raleigh’s law of radiation.

In recent years, the ideas have been developing that the law of equipartition of energy for the metallic electrons, has got to be abandoned in favour of Planck’s quantum law. The difficulty, however, lies in properly quantizing the motions of the metallic electrons and in explaining the thermal

<sup>1</sup> Read before Bangalore session of Indian Science Congress, 1923.

conductivity of metals and the correctness of Wiedemann-Franz's law on such a quantized theory. Prof. Lindemann<sup>1</sup> has pointed out that the expression 'free' electron suggesting or intending to suggest an electron normally not under the action of any force, is really a contradiction in terms. If the electrons be not attracted by atomic residues (and this assumption is essential to prevent re-combination) the repulsion between the electrons themselves will prevent their being free in the true sense. It is, therefore, conceivable that metallic electrons instead of forming an ideal gas, really constitute a condensed solid. In continuation of the conceptions of Born and Kármán, one may suppose that a metal crystal is constituted of inter-locked space lattices of electrons, atoms or atomic residues. Prof. Lindemann<sup>2</sup> has, already, chalked out a theory of metallic state on the basis of these ideas. Prof. J. J. Thomson<sup>3</sup> has, recently, developed such and similar ideas in his electron theory of solids.

The object of the present paper is to consider statistically the laws of emission of ions or electrons from hot metals on the basis of the supposition that the metallic ions or electrons behave in all manner like Planck's line vibrators while the emitted ones constitute an ideal monatomic gas.

2. *Temperature Equilibrium between the emitted Ions or Electrons with emitting Metal Crystal.*—The problem before us is to determine statistically the temperature equilibrium of a hot metal-crystal with the radiant energy of æther and with an atmosphere of gaseous ions or electrons contained in a vacuous enclosure of volume  $V$  and maintained at a temperature  $T^{\circ}A$ . The assembly for our present statistical calculations embraces various types of systems—æther, free gaseous ions or electrons, and condensed electrons,

<sup>1</sup> 'Phil. Mag.,' Vol. 29, 1915, p. 127.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Phil. Mag, Vol 48, p. 721, 1922

atoms or atomic residues in the solid state. One<sup>1</sup> can formally include all the various systems into the statistical calculations. It will, however, conduce to brevity and clearness if one assumes that the sublimation of ions or electrons takes place quite independently and does not alter the average distribution of energy amongst other systems of the assembly. The distribution of energy in any type of systems in an assembly depends on the motion of that system alone so long as it is not too frequently interfered with,—such an assumption of limited interference being fundamental to all statistical calculations.

Let us limit our considerations to any example of an assembly of  $M$  ions or electrons of which  $1, 2, \dots, N$  are in the vapour phase while  $N + 1, \dots, M$  are in the solid phase; so that the number in the solid phase is  $S = M - N$ . We will suppose that the particles in the vapour-phase form an ideal mon-atomic gas while those in the condensed state constitute Planck's resonators capable of taking energies in multiples of quanta  $\epsilon_i = h\nu_i$  ( $i = 1, 2, 3$ , etc.). The mechanism by which the resonators pass from the condensed phase to the free gaseous state, is not known. It may be either radiative or due to collision. Statistically we may suppose that  $\phi$  is the work done at the absolute zero of temperature in taking out a particle from the solid to the vapour phase. Now if  $q$ 's and  $p$ 's specify the positional and momenta co-ordinates of the gaseous particles, their energy content with respect to a standard zero state of energy, may be written as,

$$E_g = \frac{1}{2m} \sum_{i=1}^{i=3N} p_i^2 + N\phi \quad \dots \quad (1)$$

The energy of the resonators in the condensed solid phase may

<sup>1</sup> Messrs. Darwin and Fowler's new statistical method lends itself to be utilised for a more elegant treatment of the present subject. (Phil. Mag., Vol. 44, September and November, 1922; Vol. 45, January and March, 1923, and other subsequent papers).

be written in the form,

$$E_f = \sum_{i=1}^{i=3S} \epsilon_i = \frac{1}{2m} \sum_{i=1}^{i=3S} (p_i'^2 + 4\pi^2 m^2 \nu_i^2 q_i'^2) \quad \dots \quad (2)$$

where,  $\nu$ 's specify the natural frequencies of the resonators. The probability that the particles 1,2...N are in the vapour phase while N+1,...M are in the solid phase, is according to Boltzmann's theorem,

$$\omega = A f e^{-\frac{(E_g + E_f)}{kT}} (dp_1 dq_1 \dots dp_{3N} dq_{3N}) (dp'_1 dq'_1 \dots dp'_{3S} dq'_{3S}) \dots \quad (3)$$

Now, since the gaseous particles are governed by the classical laws of mechanics, we have,

$$\begin{aligned} \int e^{-\frac{E_g}{kT}} dp_1 \dots dp_{3N} dq_1 \dots dq_{3N} \\ = e^{-\frac{N\phi}{kT}} (2\pi m kT)^{\frac{3N}{2}} V^N \quad \dots \quad (4) \end{aligned}$$

where, the integration has been carried throughout the volume V (neglecting the volume of the metal crystal) from  $p=\infty$  to  $p=-\infty$ .

In order to evaluate the integral

$$\int e^{-\frac{E_f}{kT}} dp'_1 dq'_1 \dots dp'_{3S} dq'_{3S}$$

in the light of the quantum statistics, let us introduce the auxiliary variables  $\xi_i$  and  $\eta_i$  defined by,

$$\left. \begin{aligned} \xi_i &= \pi \nu_i q_i \sqrt{2m} \\ \eta_i &= \frac{p'_i}{\sqrt{2m}} \end{aligned} \right\} \quad \dots \quad (5)$$

So that we obtain

$$\epsilon_i = \xi_i^2 + \eta_i^2 \quad \dots \quad (6)$$

and hence

$$\left. \begin{aligned} \xi_i &= \sqrt{\epsilon_i} \cos \phi_i \\ \eta_i &= \sqrt{\epsilon_i} \sin \phi_i \end{aligned} \right\} \quad \dots \quad (7)$$

where,  $\phi_i$  is a parametric angle. we have thus,

$$dp'_i dq'_i = \frac{1}{\pi v_i} d\xi_i d\eta_i = \frac{1}{2\pi v_i} d\epsilon_i d\phi_i \quad \dots \quad (8)$$

$$\therefore \int \int e^{-\frac{\epsilon_i}{kT}} dp'_i dq'_i = \int \int_{\phi_i=0}^{2\pi} e^{-\frac{\epsilon_i}{kT}} d\epsilon_i \frac{d\phi_i}{2\pi v_i} = \int e^{-\frac{\epsilon_i}{kT}} \frac{d\epsilon_i}{v_i} \quad \dots \quad (9)$$

Planck's quantum statistics of the oscillators require that  $\epsilon_i$  can assume only discrete values, so that  $d\epsilon_i = h\nu_i$ . Hence the integral (9) changes to the sum,

$$\sum_{n=0}^{\infty} e^{-\frac{n h \nu_i}{kT}} \frac{h \nu_i}{v_i} = \frac{h}{1 - e^{-\frac{h \nu_i}{kT}}} \quad \dots \quad (10)$$

Hence the probability takes the form,

$$\omega = A \cdot e^{-\frac{N\phi}{kT}} (2\pi m kT)^{\frac{3N}{2}} V^N \frac{h^{3S}}{\prod_{i=1}^{3S} \left(1 - e^{-\frac{h \nu_i}{kT}}\right)} \quad \dots \quad (11)$$

where,  $\Pi_{3S}$  denotes the product of such functions as

$$\left(1 - e^{-\frac{h \nu_i}{kT}}\right) [i=1, 2, 3S].$$

Let us now consider the two special cases of relation (11).

*Case 1.* In the case of resonators for which  $h\nu_i$  is large compared to  $kT$ , we have the probability,

$$\omega = e^{-\frac{N\phi_0}{kT}} \frac{3N}{(2\pi mkT)^{\frac{3}{2}}} V^N \frac{3S}{h} \quad \dots \quad (12)$$

*Case 2.* On the other hand if the frequencies of the resonators be so low that  $h\nu_i$  is small compared to  $kT$ , we have

$$\omega = e^{-\frac{N\phi_0}{kT}} \frac{3N}{(2\pi mkT)^{\frac{3}{2}}} V^N \left( \frac{kT}{r} \right)^{3S} \quad \dots \quad (13)$$

where,  $\bar{\nu}$  is the geometric mean of the spectrum of frequencies.

Now the total number of  $M$  particles can be made into groups of  $N$  and  $S$  in  $\frac{M!}{N!S!}$  ways while the  $S$  particles inside the metal-crystal can be arranged in lattices in  $S!$  ways. Hence the total probability becomes,

$$W = \frac{M!}{N!S!} S! \omega \quad \dots \quad (14)$$

The equilibrium state of an assembly corresponds to the state of maximum probability for which we must have

$$\frac{\partial W}{\partial N} = 0 \quad \text{or} \quad \frac{\partial}{\partial N} \log W = 0.$$

Hence using Stirling's approximation in the form  $N! = N \log N - N$ , we obtain in the first case

$$\log_e \frac{N}{V} = -\frac{\phi_0}{kT} + \log_e \frac{(2\pi mkT)^{3/2}}{h^3} \quad \dots \quad (15)$$

and in the second case

$$\log \frac{N}{V} = -\frac{\phi_0}{kT} + \log_e \left( \frac{2\pi mkT}{kT} \right)^{3/2} \frac{1}{\bar{\nu}^3} \quad \dots \quad (16)$$

3. *Law of emission of Electrons.*—The electron space-lattices may possess a large number of proper frequencies and as Prof. Lindemann has pointed out, Planck's infinite number of resonators may have a physical meaning. One would, however, require special assumptions to calculate the proper frequencies of the electron space lattices. The experimental fact, namely that the electrical resistance of metals is altered only by alternating currents of very high frequencies of the order of  $10^{14}$  periods per second (as when infra-red light is reflected from metals), points to the fact that the metallic electrons must possess very high frequencies. One however does not know the lowest limit of the electronic frequencies. One may tentatively suppose that the observed frequency of the photoelectric threshold sets a limit to the lowest frequency of the metallic electrons. Ultraviolet light impinging on an electronic lattice, lets loose the electrons and projects them out. This can readily happen only when the natural frequencies of the electronic space-lattices are in resonance with the impinging light wave. In any case it is quite conceivable that metallic electrons, owing to their small mass, possess extremely high frequencies the lowest limit of which ranges from  $10^{14}$  to  $10^{15}$  for different metals. If this be so, then for the metallic electrons  $\frac{h\nu_e}{kT}$  will be much larger than unity at all temperatures available in the laboratory. Hence we can write for the equilibrium-concentration  $n_-$  of electrons near a hot metal crystal at temperature  $T^\circ A$ ,

$$n_- = \frac{(2\pi m_- kT)}{h^3} e^{\frac{3}{2} - \frac{\phi_0}{kT}} \quad \dots (17)$$

As Prof. Richardson<sup>1</sup> has pointed out, in thermionic current measurements, we do not really measure the equilibrium concentration of electrons, but the number emitted per second

<sup>1</sup> "The Emission of Electricity from Hot Bodies,"—2nd Ed., 1921, pp. 314 and 55.



per unit area of the hot body. This number  $n'_-$  is equal to  $(1-r)$  times the number reaching the body per second, where  $r$  is the fraction of the incident electrons sent back by reflection. According to the kinetic theory of gases,

$$n'_- = (1-r) n \left( \frac{kT}{2\pi m_-} \right)^{\frac{1}{2}} = (1-r) \frac{2\pi k^2 m_-}{h^3} T^2 \cdot e^{-\frac{\phi_-}{kT}} \quad \dots (18)$$

Hence the thermionic emission of electrons per second per unit area, is given by the expression,<sup>1</sup>

$$I_- = n'_- \delta = (1-r) \frac{2\pi k^2 \delta m_-}{h^3} T^2 \cdot e^{-\frac{\phi_-}{kT}} \quad \dots (19)$$

where,  $\delta$  = electronic charge.

4. *Thermionic Emission of positive Ions.*—The positive ions, owing to their larger mass, would possess much lower frequencies and for temperatures within the range 1000°A to 2000°A, one may reasonably suppose that  $h\nu_i$  is small compared to  $kT$ , and so we have for the equilibrium-concentration of positive ions,

$$n_+ = \left( \frac{2\pi m_+}{kT} \right)^{3/2} \frac{1}{\nu_+} e^{-\frac{\phi_+}{kT}} \quad \dots (20)$$

The thermionic emission of positive ions per second per unit area is

$$I_+ = \left( \frac{2\pi m_+}{k} \right)^{3/2} \delta \frac{\nu_+}{T^2} e^{-\frac{\phi_+}{kT}} \quad \dots (21)$$

In the absence of any further knowledge of  $\nu$ , we cannot put expression (21) to an experimental test. But the relation (19) contains no unknown constants except the work-function

<sup>1</sup> Laue has worked out the same expression by thermodynamical arguments (Jahrb. d. Radioaktivität 15, 205 U 257, 1918; and Ann der Phys. Vol. 58, 1919, p. 695). Dushman, Phys. Rev., June, 1923.

$\phi_-$  a knowledge of which should enable us to predict theoretically the rate of emission of electrons from different metals at various temperatures under perfect vacuum conditions.

5. *The Nature of the work-function  $\phi_-$ .*—The fact that the emission of electrons is attended by a cooling effect while absorption results in a heating effect, suggests that the emission may be regarded as a process of sublimation of electrons from the solid to the gaseous phase and we can designate  $\phi_-$  in heat units as the 'heat of sublimation' or 'heat of condensation' of electrons at the absolute zero of temperature. On the other hand this work-function in equivalent volts should be analogous to the ionisation potential of gases and vapours. The recent work of Compton and others on low voltage arcs in gases and vapours, has brought to light the interesting fact that the ionisation potentials of vapours are not constant but may be much less for atoms brought to an abnormal condition by absorption of radiation generated in other atoms. The ionisation potential therefore may be shifted back to the first resonance potential as its limiting value. The closeness of atoms in the condensed state will certainly loosen the electrons on the surface of the atoms. We should, therefore expect the ionisation potentials of elements in the condensed state to be much diminished. It is unfortunate that we know very little as yet about the exact nature of 'loosening' of the electrons inside a metal, or about the mechanism of emission, which may be either radiative or due to collision. It is however quite probable that both radiation and collision are simultaneously operative in the actual processes involved. But it would introduce much simplification into the theory if one single mechanism could explain the emission. The argument against the view that the thermionic emission may be regarded as due to the radiation of the hot body itself is that the magnitude of the auto-photo-electric currents is much lower than the thermionic currents. This is, however, to be expected. For by impinging

radiation from outside on metals, we do not really attain to the condition of radiation due to the hot body itself. If thermionic emission of electrons were due to the radiation of the hot body itself, then the type of arguments advanced by Prof. Richardson<sup>1</sup> in his statistical theory of photo-electric effect, should apply to the case of thermionic emission. According to his statistical theory the average kinetic energy of electrons emitted by radiation of frequency  $\nu$  is given by,

$$\bar{T} = h\nu - \phi \quad \dots (22)$$

Hence for electrons emitted with zero kinetic energy, we should have,

$$0 = h\nu_0 - \phi_0 \quad \dots (23)$$

where,  $\nu_0$  is the frequency of the photo-electric threshold. There is no *a priori* reason why  $\phi_0$  and  $\phi_-$  should not be identical. But the experimental observations on both thermionic and photo-electric effects are so hopelessly conflicting and uncertain that no one can as yet pronounce any decision on this point with any degree of certainty. It appears to me that if some theoretical expression could be found for the calculation of the long-wave-length limit, it might serve some useful end in this connection. One such way is indicated below. Prof. Richardson's <sup>2</sup> statistical theory of photo-electric effect leads to the relation,

$$\nu_0 = \frac{2}{3}\nu_m \quad \dots (24)$$

where  $\nu_m$  is the frequency of the maximum selective photo-electric effect. Prof. J. J. Thomson<sup>3</sup> in his recent developments of the electron theory of metals, has given us a method of calculating the frequency of the selective photo-electric

<sup>1</sup> Phil. Mag., Vol. 23, p. 594, 1912; Vol. 25, p. 574, 1912.

<sup>2</sup> Loc. cit.

<sup>3</sup> Loc. cit.

effect. In the case of monovalent alkali metals,

$$\nu_m = \frac{(5 \cdot 224)^{\frac{1}{2}}}{2\pi m^{\frac{1}{2}}} \delta \left( \frac{A}{M} \right)^{\frac{1}{2}} = 4 \cdot 526 \times 10^{15} V^{\frac{1}{2}} \quad \dots (25)$$

where  $V$  is the atomic volume of the elements. Combining (24) and (25), we obtain an expression for the long-wave-length limit of alkali metals in the form,

$$\lambda_0 = 9942 \times 10^{15} V^{\frac{1}{2}} \text{ cms} \quad \dots (26)$$

This expression appears to apply quite satisfactorily to a large number of metals irrespective of any question of valency. But to assume that the electronic structure of all these metals is the same as that of alkali metals is certainly far from convincing. One should, however, find no difficulty in working out similar expressions for polyvalent metals with different arrangements of electrons on the lines indicated by Prof. J. J. Thomson. The multiplying factor of  $V^{\frac{1}{2}}$  in the expression (26) on numerical computation, however, yields nearly the same value with various different arrangements of electrons except for the divalent elements. Apart from the question of valency and structure, the validity of such calculations of  $\lambda_0$  rests on the assumption of the existence of selective photo-electric effect in all metals. One does not know whether the selective effect is due to peculiarly numerous proper frequencies within a small region or due to other intra-atomic electrons. In any case, there is, *a priori*, no reason why all metals should not show selective photo-electric effect.

In the following pages are given certain calculations based on the photo-electric and thermionic data of various reliable observers to test the identity of photo-electric and thermionic work-functions.

6. *Method of calculations.*—For most metals  $r$  has the value <sup>1</sup>  $\cdot 5$  nearly. And since the exponential factor in the expression for emission is relatively more important, the percentage of error introduced in the value of  $I_-$  will be inappreciable on putting  $r$  equal to  $\cdot 5$  even in cases of metals in which its value differs from this by a small amount. Hence taking  $r = \cdot 5$  generally in the expression (19), we have,

$$I_- = \frac{\pi m_e e k^2}{h^3} T^{\frac{3}{2}} e^{-\frac{\phi_-}{kT}} = A T^{\frac{3}{2}} e^{-\frac{b}{T}} \quad \dots \quad (27)$$

using the values,

$$k = 1 \cdot 372 \times 10^{-16} \text{ ergs/deg.}$$

$$h = 6 \cdot 55 \times 10^{-27} \text{ erg/sec.}$$

$$m = 8 \cdot 995 \times 10^{-28} \text{ grams.}$$

$$e = 4 \cdot 774 \times 10^{-10} \text{ E S U}$$

we have,

$$A = 9 \times 10^{10} \text{ E S U/cm}^2 \text{ deg}^{\frac{3}{2}}.$$

$$= 30 \cdot 1 \text{ amp/cm}^2 \text{ deg}^{\frac{3}{2}}$$

$$\therefore I_- = 30 \cdot 1 T^{\frac{3}{2}} e^{-\frac{b}{T}} \quad \dots \quad (27)$$

$$\log_{10} I_- = 1 \cdot 4786 + 2 \log_{10} T - \frac{b}{2 \cdot 303 T} \quad \dots \quad (28)$$

Thermionic work-function,

$$\phi_{\text{therm}} = \frac{hb}{e} = \cdot 862 \times 10^{-4} b \text{ volts} \quad \dots \quad (29)$$

Photo-electric work-function,

$$\phi_{\text{phot}} = \frac{h\nu_0}{e} = \frac{12 \cdot 36}{\lambda_0} \times 10^{-5} \text{ volts} \quad \dots \quad (30)$$

<sup>1</sup> A. Gehlts (Ann. d. Phys., 36, 995, 1911).

where  $\lambda_0$  is the long wave-length limit of the metals in centimeters.

7. *Comparison of theoretical and experimental values.*

HEAVY METALS.

1. *Platinum.*—The experimental determination of the long wave-length limit of platinum has been made by different investigators. Otto Koppius<sup>1</sup> gives the value  $257\mu\mu$  for  $\lambda_0$ , Messrs.<sup>2</sup> Kober, Sende and Simon have found the value to lie somewhere between  $260\mu\mu$  to  $300\mu\mu$  some of their determinations being at  $283\mu\mu$  and  $285\mu\mu$ . Richardson<sup>3</sup> and Compton's determination from the maximum energy of the photo-electron fixes the value at  $280\mu\mu$ , while that from the mean energy leads to the value  $291\mu\mu$  for  $\lambda_0$ . The two observers, however, consider that their determinations from the mean energies are more accurate. Taking all these facts together one can reasonably suppose that  $291\mu\mu$  is the most probable value for the long wave-length limit for platinum. According to Richardson-Thomson rule,

$$\begin{aligned}\lambda_0 &= .9942 \times 10^{-5} V^{\frac{1}{2}} \text{ cms} \\ &= 296\mu\mu.\end{aligned}$$

Below are given R. Suhrmann's<sup>4</sup> and W. Schlichter's<sup>5</sup> data on emission from platinum under the best vacuum conditions.

R. Suhrmanu's data on emission from platinum.

Length of the Pt-foil =  $21 \text{ mm}$ .

Breadth of the foil =  $2 \text{ mm}$ .

$$I = \frac{2.31 \times 10^{-7}}{\text{area}} n = 5.5 \times 10^{-7} n \text{ amp}$$

$$h_0 = 2.303 T(1.4786 + 2 \log_{10} T - \log_{10} I)$$

<sup>1</sup> Phys. Rev., Vol. XVIII, No. 6, 1921.

<sup>2</sup> Dissertation Dresden, 1917 (Auszug Phys. Zeitsche), 8562-563, 16, 595, 1915.

<sup>3</sup> Phil. Mag., XXIV, p. 578, 1912.

<sup>4</sup> Zeits f. Physik, 13, 1 and 2, pp. 17-34, 1923.

<sup>5</sup> Ann. der Phys., Vol. XLVII, p. 573, 1915.

TABLE I.

T°A	<i>n</i>	<i>I</i>	$\log_{10} I$	$\log_{10} I$	<i>b<sub>0</sub></i>
1750	5.8	$3.19 \times 10^{-6}$	3.1959	-6 + .5038	48330
1604	11.8	$6.49 \times 10^{-6}$	3.2051	-6 + .8122	48300
1639	22.2	$1.221 \times 10^{-5}$	3.2146	-5 + .0867	48300
1672	42.2	$2.321 \times 10^{-5}$	3.2232	-5 + .3657	48360
1689	58.0	$3.190 \times 10^{-5}$	3.2277	-5 + .5038	48350
1722	96.6	$5.313 \times 10^{-5}$	3.2360	-5 + .7253	48500
1739	121.6	$6.688 \times 10^{-5}$	3.2402	-5 + .8253	48580

$$\text{mean } b_0 = 48480$$

$$\phi_{\text{therm}} = 4.18 \text{ volts.}$$

$$\therefore \lambda_0 = 295.7 \mu\mu$$

W. Schlichter's data on Emission from platinum.

Area = 23 cm<sup>2</sup>.

TABLE II.

T°A	<i>J</i>	<i>I</i>	$\log_{10} I$	$\log_{10} I$	<i>b<sub>0</sub></i>
1195	$1.5 \times 10^{-9}$	$6.5 \times 10^{-11}$	3.0774	-11 + .8129	49060
1227	$7.8 \times 10^{-9}$	$3.4 \times 10^{-10}$	3.0888	-10 + .5315	48370
1243	$1.35 \times 10^{-8}$	$5.9 \times 10^{-10}$	3.0944	-10 + .7709	48480
1291	$6.30 \times 10^{-8}$	$2.74 \times 10^{-9}$	3.1109	-9 + .4378	48340
1355	$4.70 \times 10^{-7}$	$2.04 \times 10^{-8}$	3.1319	-8 + .3096	48180
1403	$1.68 \times 10^{-6}$	$7.30 \times 10^{-8}$	3.1470	-8 + .8633	48190
1451	$5.50 \times 10^{-6}$	$2.39 \times 10^{-7}$	3.1617	-7 + .3784	48220
1499	$1.43 \times 10^{-5}$	$6.22 \times 10^{-7}$	3.1759	-7 + .7938	48450

$$\text{mean } b_0 = 48410$$

$$\phi_{\text{therm}} = 4.173 \text{ volts.}$$

$$\therefore \lambda_0 = 296.2 \mu\mu.$$

2. *Tungsten*.—Davission<sup>1</sup> and Germer's emission data for Tungsten filament. Area=0.1825 cm<sup>2</sup>.

TABLE III.

<sup>3</sup> T°A	J	I	log <sub>10</sub> T	log <sub>10</sub> I	b <sub>0</sub>
1923	9.341 × 10 <sup>-5</sup>	5.12 × 10 <sup>-4</sup>	3.2840	-4 + .7091	50200
1973	1.973 × 10 <sup>-4</sup>	1.01 × 10 <sup>-3</sup>	3.2952	-3 + .0340	50160
2021	3.967 × 10 <sup>-4</sup>	2.12 × 10 <sup>-3</sup>	3.3056	-3 + .3373	50050
2069	7.656 × 10 <sup>-4</sup>	4.20 × 10 <sup>-3</sup>	3.3158	-3 + .6228	49960
2113	1.362 × 10 <sup>-3</sup>	7.46 × 10 <sup>-3</sup>	3.3249	-3 + .8729	49780
2162	2.588 × 10 <sup>-3</sup>	1.39 × 10 <sup>-2</sup>	3.3349	-2 + .1433	49790
2207	4.450 × 10 <sup>-3</sup>	2.42 × 10 <sup>-2</sup>	3.3438	-2 + .3828	49720
2247	6.875 × 10 <sup>-3</sup>	3.77 × 10 <sup>-2</sup>	3.3516	-2 + .5761	49720
2298	9.792 × 10 <sup>-3</sup>	5.37 × 10 <sup>-2</sup>	3.3613	-2 + .7297	50100

mean b<sub>0</sub>=49942.

φ<sub>therm</sub>=4.30 volts

∴ λ<sub>0</sub>=287.5 μμ

Calculated from Langmuir's<sup>3</sup> data, b<sub>0</sub>=44200, and φ<sub>therm</sub>=4.23 volts and hence λ<sub>0</sub>=292.2 μμ. The atomic volume of Tungsten is a little greater than that of platinum. Hence λ<sub>0</sub> for Tungsten should be greater than that for platinum. The only direct observation of the long wave-length-limit of Tungsten is due to M. J. Kelley and Hagenow<sup>4</sup> and the indication of their experiment is that the wave-length of the photo-electric threshold is near about 230 μμ. This result probably gives us only a preliminary idea of the magnitude of the long wave-length limit for Tungsten. Mr. K. K. Smith's<sup>5</sup> thermionic current measurements are, however, in good agreement with Richardson-Thomson rule.

<sup>1</sup> Phys. Rev., Vol. XX, 1922.

<sup>2</sup> Langmuir's temperature scale has been accepted.

<sup>3</sup> Phys. Zeit. Jahrg. 15, p. 525, 1914.

<sup>4</sup> Phys. Rev., Vol. XIII, No. 6, p. 15, 1919.

<sup>5</sup> Phil. Mag., Vol. XXIX, p. 811, 1915.



## Mr. K. K. Smith's emission data on Tungsten—

TABLE IV.

T°A	i	$\log_{10} T$	$\log_{10} I$	$b_0$
1100	$2.56 \times 10^{-12}$	3.0414	$-12 + .4282$	48460
1200	$1.69 \times 10^{-10}$	3.0792	$-10 + .2279$	48140
1300	$5.83 \times 10^{-9}$	3.1139	$-9 + .7657$	47720
1400	$1.22 \times 10^{-7}$	3.1461	$-7 + .0864$	47350
1500	$1.70 \times 10^{-6}$	3.1761	$-6 + .2304$	47000
1600	$1.71 \times 10^{-5}$	3.2041	$-5 + .2330$	46630
1700	$1.32 \times 10^{-4}$	3.2304	$-4 + .9079$	46500
1900	$1.88 \times 10^{-3}$	3.2783	$-3 + .2742$	47100
2100	$6.70 \times 10^{-3}$	3.3011	$-2 + .8260$	45130
2300	$6.74 \times 10^{-1}$	3.3619	$-1 + .5265$	46010

mean  $b_0 = 47010$ . $\phi_{\text{therm}} = 4.05$  volts. $\lambda_0 = 300.2 \mu\mu$ .

According to Thomson-Richardson law,

$$\lambda_0 = .9942 \times 10^{-5} \times \left( \frac{183}{19.2} \right)^{\frac{1}{2}} \text{ cms}$$

$$= 306.2 \mu\mu.$$

$$\therefore \phi_{\text{phot}} = 4.03 \text{ volts.}$$

3. *Tantalum*.—The long wave-length-limit of Tantalum has not been directly observed. But according to Thomson-Richardson law

$$\lambda_0 = .9942 \times 10^{-5} \left( \frac{181.5}{16.6} \right)^{\frac{1}{2}} = 328.3 \mu\mu$$

$$\phi_{\text{phot}} = 3.77 \text{ volts.}$$

Computed from Langmuir's<sup>1</sup> thermionic data of Tantalum,  $\phi_{\text{therm}} = 4.03$  volts, which corresponds to  $\lambda_0 = 307 \mu\mu$  nearly.

<sup>1</sup> Phys. Rev., Vol. II, p. 450, 1913.

Suhrmann's<sup>1</sup> very recent emission data of Tantalum are however, in very good agreement with Thomson-Richardson rule.

$$I_- = 5.5 \times 10^{-7} n \text{ amps.}$$

TABLE V.

T°A	n	I	log <sub>10</sub> T	log <sub>10</sub> I	b <sub>0</sub>
1440	8.0	...	3.1584	-6 + .6435	43610
1497	22.0	...	3.1753	-5 + .0828	43950
1549	59.2	...	3.1900	-5 + .5127	44020
1600	130.0	...	3.2041	-5 + .8543	44220
1628	190.0	..	3.2116	-4 + .0192	44520
1651	273.0	..	3.2178	-4 + .1766	44650
1679	370.0	...	3.2251	-4 + .3016	44870

$$\text{mean } b_0 = 44400.$$

$$\phi_{\text{therm}} = 3.82 \text{ volts.}$$

$$\therefore \lambda_0 = 323.4 \mu\mu.$$

Langmuir's and other observer's emission data on Molybdenum, Thorium, etc., have been tested in the same manner. They are not elaborately dealt with here, so as not to extend this paper unduly. The computed results will, however, be included in a table at the end of this paper.

### ALKALI METALS.

Both photo-electric and thermionic experiments on the alkali metals are extremely difficult on account of the great susceptibility of these metals to contamination. While many attempts have been made to determine the frequencies of the photo-electric thresholds and also of the selective effects, the results obtained by the various investigators are very discordant. On the other hand, very few attempts have been made to study

<sup>1</sup> *Loc. cit.*

the thermionic emission of electrons from these metals. Nevertheless, we must test the applicability of the present law with whatever experimental data we have at our disposal at present.

### 1. *Sodium* :—

Observers	$\lambda_m$	$\lambda_0 = \frac{3}{2}\lambda_m$
1 Pohl and Pringsheim <sup>1</sup>	320 $\mu\mu$ —340 $\mu\mu$	480 $\mu\mu$ —510 $\mu\mu$
Richardson and Compton <sup>2</sup>	360 $\mu\mu$	540 $\mu\mu$
Richtmeyer <sup>3</sup>	460 $\mu\mu$	690 $\mu\mu$

But according to Thomson's theory  $\lambda_m$  is 324 $\mu\mu$  which corresponds to a value 486 $\mu\mu$  only for  $\lambda_0$ . Thomson-Richardson law, therefore, appears to have failed in correctly representing the characteristic photo-electric behaviour of sodium. Such a conclusion would, however, be superficial. For this law is in good quantitative agreement with the photo-electric measurements on all other alkali-metals. It is conceivable, however, that sodium contains oscillators possessing natural frequencies of two or more particular values so that the emission might be maximum at two or more points, when the stimulating frequency might be greater or equal to the characteristic frequencies.

One could naturally suppose that the direct determination of the long wave-length-limits of sodium might lead to some decision on the point. But one is simply disappointed by the widely discordant result of the different investigators.

Observers.	$\lambda_0$
Richardson and Compton <sup>4</sup>	577 $\mu\mu$ —583 $\mu\mu$
Souder <sup>5</sup>	>623·5 $\mu\mu$
Millikan <sup>6</sup>	680 $\mu\mu$

<sup>1</sup> Verh. d. Deutsch. Phys. Ges, XI, r. 1039, 1910.

<sup>2</sup> Phil. Mag., 26, 549, 1913.

<sup>3</sup> Phys. Rev., Vol. XXX, 3, 1910.

<sup>4</sup> Phil. Mag., 26, 549, 1918.

<sup>5</sup> Phil. Mag., 25, p. 576, 1912.

<sup>6</sup> Phys. Rev., Vol. VII, 1st series, 1916.

Observers.	$\lambda_0$
Richtmeyer <sup>1</sup>	598 $\mu\mu$ —633 $\mu\mu$ .

If one accepts Richardson and Compton's value 583 $\mu\mu$  for  $\lambda_0$ ,  $\phi_{\text{phot}}$  becomes 2.12 volts.

The only thermionic data on sodium are due to Fredenhaagen and Richardson. Fredenhaagen failed to remove gaseous contaminations and his results are, therefore, useless for a quantitative test of the present theory. Richardson's experiments on sodium are also not very reliable. He obtained thermionic currents of the order  $10^{-6}$  amperes per sq. cm. at 500°C. Calculated from his data,  $\phi_{\text{therm}}$  comes out to be 2.01 volts. The order of correspondence between the theory and the observations of the various investigators is not very unsatisfactory. Yet it appears as if this alkali has kept concealed in itself some mystery yet unrevealed.

2. *Cæsium*.—Very little is known about the photo-electric behaviour of this alkali. According to Cornelius's <sub>2</sub> observations  $\lambda_0$  is greater than 750 $\mu\mu$ . Pohl and Pringshein <sup>3</sup> gives the value 550 $\mu\mu$  for  $\lambda_m$  which corresponds to a value 825 $\mu\mu$  for  $\lambda_0$ . According to Thomson-Richardson law,

$$\begin{aligned}\lambda_0 &= .9942 \times 10^{-5} \times \left( \frac{132.8}{1.87} \right)^{\frac{1}{2}} \text{ cmz} \\ &= 838 \mu\mu \\ \phi_{\text{phot}} &= 1.47 \text{ volts.}\end{aligned}$$

Calculated from Langmuir's <sup>4</sup> recent data for emission from cæsium,  $b$  is 15930 and hence  $\phi_{\text{therm}}$  is equal to 1.38 volts. The agreement between  $\phi_{\text{therm}}$  and  $\phi_{\text{phot}}$  for cæsium is quite good. The absence of any thermionic data for other alkali metals handicaps me in examining them in the light of the present theory.

<sup>1</sup> Phys. Rev., Vol. XXX, No. 3, 1910.

<sup>2</sup> Phys. Rev., 1913, Vol. 1, second series.

<sup>3</sup> Loc. cit.

<sup>4</sup> Science, 57, pp 58-60, Jan. 1923.

A summary of the computed values of  $\phi_{\text{therm}}$  and the characteristic photo-electric constants either calculated according to Thomson-Richardson law or directly observed, is given below for comparison.

TABLE VI.

Metallic elements.	THERMIONIC.		PHOTO-ELECTRIC.		RICHARDSON-THOMSON RULE.	
	$\phi_{\text{therm}}$ in volts.	$\lambda_0$ in $\mu\mu$	$\lambda_m$ in $\mu\mu$ (obs.).	$\lambda_0$ in $\mu\mu$ (obs.).	$\lambda_m \mu\mu$	$\lambda_0 = \frac{3}{2} \lambda_m \mu\mu$
Pt	4.18 (Suhrmann) 4.17 (Sehlichter)	$\left\{ \begin{array}{l} 295.7 \\ 296.2 \end{array} \right\}$	...	291 (Richardson)	197.3	296
W	4.23 (Langmuir) 4.05 (Smith)	$\left\{ \begin{array}{l} 292.2 \\ 300.2 \end{array} \right\}$	...	230 (Kelley)	205.0	307
Mo	3.93 (Longmuir)	315.1	...	...	215.3	323
Ta	3.82 (Suhrmann)	323.4	...	...	218.7	328
Th	2.74 (Langmuir)	451.1	...	...	304.7	457
Na	2.09 (Richardson)	614.9	$\left\{ \begin{array}{l} 320-340 \text{ (Pohl, etc.)} \\ 460 \text{ (Richtmeyer)} \end{array} \right\}$	$\left\{ \begin{array}{l} 583 \text{ (Richardson)} \\ 598-633 \text{ (Richtmeyer).} \end{array} \right\}$	324	486
K	...	...	440 (Pohl, etc.)	...	446	669
Rb	...	...	480 ditto	...	494	741
Cs	1.38 (Langmuir)	896	550 ditto	>750 (Comelius)	559	838
C	4.52 (Langmuir) 4.51-4.97 (Pring and Parker).	$\left\{ \begin{array}{l} 274 \\ 250-275 \end{array} \right\}$	...	255-260 (Hughes)	168.178	252.257

*Concluding remarks.*—It would be premature at present to pronounce any definite opinion on the question of identity between photo-electric and thermionic work functions, specially in view of the uncertainties in the determinations of the long wave-length-limits. The data collected in Table VI, however, points to a general correspondence between the two. The universal applicability of the Richardson-Thomson rule, used here empirically to a large number of metals, is probably doubtful. But it certainly indicates the possibility of a

theoretical estimation of the long-wave-length limits from the space-lattice arrangements of electrons in different metals.

The thermionic work-function  $\phi_-$  in volts may be looked upon as the sum of two potentials  $\mu_-$  and  $\psi_-$ .<sup>1</sup>  $\mu_-$  is the electron-affinity inside a metal, and is essentially related to the nature of electron-binding with atoms or atomic residues.  $\psi_-$  is the surface-potential of the metal and is due to the work which an electron has got to do in escaping from the surface of the metal against the force of attraction of its image-point which at a distance  $d$  from the surface is equal to  $\frac{\delta}{4d}$ .<sup>2</sup> It is, of course, implied that the concentration of the emitted electrons is so low that any potential difference arising out of their space-charge is negligible. If the emission becomes copious, the space-charge potential cannot be dismissed as being negligible.

Russel has pointed out that the ionisation potential of gases and vapours is a periodic function of the atomic number. One would, therefore, expect the same remark to apply to the ionisation potentials of elements in the condensed phase.<sup>3</sup> Now whatever view be taken of the thermionic work-function, the figures in column I of Table VI, appear to make it abundantly clear that the work-function  $\phi_-$  is a function of the atomic volume.

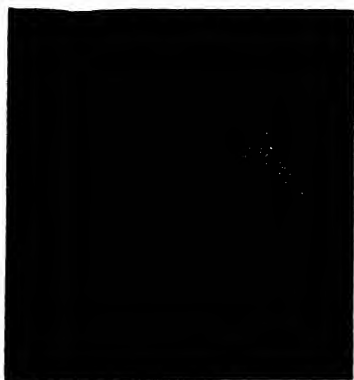
<sup>1</sup> W. Schottley, Zeit.

<sup>2</sup> Phys. 14, 63, 1923.

<sup>3</sup> Astr. Phys. Journ., Vol. VI, 1922.

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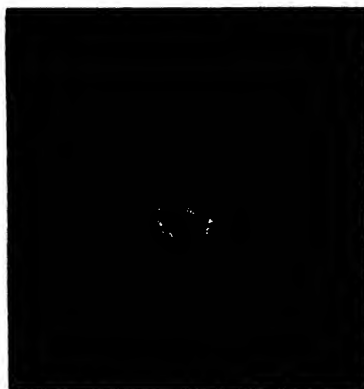
PLATE I



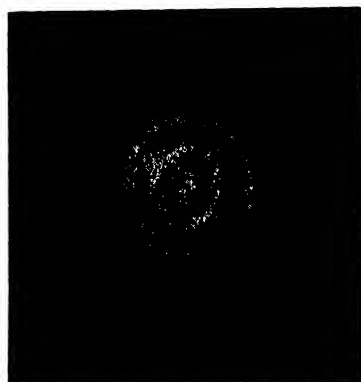
1



2



3



4

RINGS SHOWN BY REFLECTED AND SCATTERED LIGHT.

# On the colours shown by “Nobili's Rings.”

By

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## INTRODUCTION.

When a polished plate of platinum, silver or brass, connected with one pole of a battery is immersed horizontally in a suitable electrolytic solution and a vertical wire of platinum connected with the other pole is held in the solution about a millimetre distant from the plate, then on passing a strong current through the circuit so made, beautiful rings are formed upon the plate with the platinum point as the centre. Such rings were noticed first by Nobili<sup>1</sup> and since then they have been obtained by Schönbein<sup>2</sup> with a passive iron wire as the positive pole in a lead acetate solution and by Fechner<sup>3</sup> upon a silver plate using a solution of copper acetate and a zinc wire point as one electrode. Later on Becquerel<sup>4</sup> obtained the rings on a German silver plate. The rings obtained with copper sulphate solution were not much coloured, but those obtained employing other solutions showed beautiful colours, and Becquerel observed that the rings showed colours like Newton's rings in white light and from that similarity he proceeded to determine the diameter of the rings from the consideration of the current

<sup>1</sup> Nobili-Bibl. Univ. 33, p. 302, 1826.

Pogg Ann., 10, p. 392, 1827.

<sup>2</sup> Schönbein—Pogg Ann., 40, p. 421, 1837

<sup>3</sup> Fechner—Schweigg Journ. 55, p. 442, 1829.

<sup>4</sup> Becquerel—Ann de chim et de phys (3) 13, p. 342, 1845 Archives l' El 4, p. 82.



density about the platinum electrode. His results were verified by Beetz <sup>1</sup> later on.

Although the phenomenon was observed so many years ago, yet no satisfactory explanation about the origin of such beautiful colours in those rings seems to have ever been attempted. The similarity of colour sequence in these rings to the white light Newton's rings, suggested the explanation that here also we had the phenomena of interference and the colours are due to the interference of light by thin films deposited upon the metal plate whose thickness diminished as one moved away from the centre, the point just below the vertical electrode.

The present author in a previous paper <sup>2</sup> made a complete study of the Colours shown by tempered metal surfaces. As the colours in the present instance have many properties in common with the colours shown by heated metal surfaces, it at once suggested that the underlying cause may be the same in both phenomena. In the present investigation, an attempt has been made to explain the colours from the stand point that the films deposited upon the metal plates for the formation of Nobili's rings during electrolysis are discontinuous and granular in structure and hence the colours must originate from the scattering of light by those granular particles upon a polished metal surface.

## 2. PRODUCTION OF NOBILI'S RINGS.

The proper metal plate for the production of rings is to be selected. In fact different metal plates have been employed by different investigators in connection with different solutions. The present author tried to get rings with saturated solutions of copper sulphate, lead sulphate and manganous sulphate and plates of brass, silver, copper

<sup>1</sup> Beetz—Pogg Ann. 71, p. 79, 1847.

“ “ 97, p. 22, 1856.

<sup>2</sup> B. N. Chuckerbutti—Proc. of Ind. Assoc. for the Cultivation of Science, Vol. VII, Parts III and IV, 1922.

and aluminium. The rings are very beautifully obtained in cases where the metal plate is connected with the negative terminal of the battery.

In experiments with copper sulphate solution, the rings obtained upon a brass plate are almost colourless, there being dull-red rings of copper separated by brighter intervals. But some colouration is obtained, however, when sufficient time is allowed for the oxidation, in contact with air, of the liberated metal during the interval between the taking out of the plate from the solution and cleansing by tap water. Such colours are however formed only at places sufficiently removed from the centre because it is there that we should expect small particles not yet set upon the metal bed, whereas the layers near the centre are not affected at all. It was possible however to get an entire set of coloured rings in the case of copper sulphate solution and a negative plate of silver by allowing the current to pass for a very short time and then taking out the plate immediately. The succession of colour in such rings was from the centre outwards—dull-red, yellow, green, violet. The rings obtained with lead sulphate solution and a negative brass plate, however, surpass all description in gorgeousness of colour. About four or five complete rings were distinguishable. The arrangement of colours was from the centre outwards—dull-red, yellow, bluish-green, violet-red, green-yellow, blue and reddish violet. Similar coloured rings were also obtained with manganous sulphate solution and a negative brass plate.

In the case of negative aluminum plate in a copper sulphate solution, the alternate rings of metallic copper are beautifully seen against the whitish back-ground. But it requires rather a greater time for the formation of rings in this case than in the cases cited before. Attempts were also made with a copper plate. But in this case although the deposition was in alternate rings, the contrast was not good and moreover the rings were very near together.

The current to be employed in all these cases should be sufficiently high and the whole phenomenon is complete within 10 to 15 seconds. A feeble current gives only a deposit without formation of any definite rings. The current employed in all cases was about 2 amperes from a main of 220 volts.

For the best production of coloured rings it is essential that the metal surface should be highly polished. It is impossible to get the well-coloured rings with a rough surface, but only a nonuniform deposit is obtained. Another important point for success in these experiments is that the vertical electrode should be as near the plate as possible but never touching it. For, otherwise, although the other conditions might be satisfied, no rings are formed even if the current is passed for a sufficient time.

### 3. MICROSCOPIC OBSERVATION OF THE METAL PLATES.

That the structure formed upon the metal surface during electrolysis is not continuous but granular, can be seen at once if the plates be subjected to a microscopic study. The difficulty lies in the fact that the metal surface being in the background, the granules cannot properly be illuminated. The difficulty can, however, be overcome by employing light from a high candle power source incident very obliquely upon the plate. Beginning the observations from the centre of the ring system to the farther side, the variation in the nature of the structure in different parts is marvellously shown. At a distance are found the minute particles quite separate from one another but sometimes forming clusters. But as the centre of the system is approached little by little, the size of the particles also increases. It should be noted, however, that the regions of bigger particles are not quite free from the presence of smaller granules so common at the distance. It is possible to measure the size of the granules with the help of a micrometer eyepiece. Thus for the smallest

particles the diameter comes out to be  $275\mu\mu$  (or  $ka=1.35$ , where  $k=\frac{2\pi}{\lambda}$ ,  $a$  is the radius of the particle,  $\lambda$ =wave-length of light) and for the biggest particles obtained, the diameter comes out to be  $500\mu\mu$ . Thus the size of the particles obtained in the present circumstances is of the same order of magnitude as the particles formed upon a heated metal surface.<sup>1</sup>

#### 4. DETAILED STUDY OF THE PHENOMENA OBSERVED.

##### (A) *Colour and Polarisation of Reflected Light.*

If a beam of white light is allowed to fall upon the ring systems and the reflected light observed then, the colour and polarisation of the reflected light vary with the angle of incidence and the position of the ring, in a very remarkable way. On viewing the reflected light with the naked eye the reflected colours are most lively at or about normal incidence, and become less and less saturated as the obliquity of incidence is increased and, at very oblique incidence, it is impossible to distinguish the colours in the different rings, the proportion of white light reflected being very great.

On employing a nicol for observation it is found that at small obliquities only the last two rings are affected in colour and intensity as the nicol is rotated about its axis, but the rings near the centre show no appreciable change at all. At more oblique incidences, however, the colour of the rings near the centre show striking changes as the nicol is rotated from one position (namely, principal plane perpendicular to the plane of incidence) to the position normal to it. Thus, in the first position of the nicol the colours are vivid but less intense and in the second position their intensity increases but they become less strongly coloured. It is further to be noted that for oblique incidences the colours observed in the two positions of the nicol are complementary to each other.

<sup>1</sup> B. N. Chuckerbutti, *loc. cit.*, p. 80.

The arrangement of colours in the ring system observed in reflected white light incident normally, upon the Nobili's rings formed upon a brass plate with lead sulphate solution is as follows.

Centre—Dull red.

First ring—Yellow, bluish green.

Second ring—Green, Violet-red.

Third ring—Green yellow, blue, Reddish-violet.

*(B) Colour and Polarisation of the Scattered light.*

It is a very important feature of the deposits upon metal plates which give rise to Nobili's rings that they scatter light very profusely. As a general rule, it may be observed that the colour of the scattered light in directions near about that of the regularly reflected light is complementary to it. The behaviour of the scattered light for various angles of observation, when white light is incident normally, can be observed with a certain amount of exactitude, if the plate be mounted normally upon the table of a Cornu polarimeter fitted with an analyser and also polariser. The apparatus is essential in such experiments and also in other experiments on the polarisation of light. The observations may be divided under two heads as follows :—

(i) *Polarised White Light incident normally.*—When polarised white light is incident normally upon the rings, the scattered light in directions very near to the direction of the normal to the plate cannot be quenched in any position of the analysing nicol but the intensity shows fluctuation as the nicol is rotated through various positions. But at angles very near to the surface the colours can entirely be quenched by the analysing nicol but re-appear again on further rotating the nicol. In viewing with the naked eye, it is found that the colours in different rings take up different tints, as the angle of observation is changed.

(ii) *Unpolarised white light incident normally.*—In viewing with the naked eye in directions contiguous to the plane of the plate, the number of rings distinguishable is not very great but as the angle is increased most of the colours come to view. As one proceeds towards the normal to the plate the colours of the rings pass through several fluctuations and in directions near about the direction of the regularly reflected light, the colours in the rings are complementary to those of the scattered light.

The scattered light shows first traces of polarisation at an angle of about  $60^\circ$  with the normal. In that position the colour of the external big rings shows the complementary tint on rotating the analysing nicol through a right angle but the colours of the inner rings are not affected much. Then from that position as the direction of the surface of the plate is approached, the colour of all the rings changes remarkably on the rotation of the nicol.

## 5. EXPLANATION OF THE PHOTOGRAPHS.

The Photographs (Plate I) were obtained to show the complementary nature of the reflected and scattered light in certain directions. To obtain these, light from a 1,000 candle-power electric lamp after passage through a monochromator ( $\lambda=6260$  A. U.) was made to fall upon the plate containing the rings. Two such metal plates were used, namely, the brass plate showing the rings due to lead sulphate solution, and also the brass plate showing the rings due to copper sulphate solution. Figs. 1 and 2 give the photographs of the rings on the first metal plate by the regularly reflected light and the scattered light in a direction near about to that of the reflected light, respectively. Similarly, Figs. 3 and 4 show the rings due to copper sulphate solution in the reflected and scattered light respectively. On account of the feebleness of the scattered light, the negatives were not much dense even after an exposure for twelve hours. The contrast is thus

not very clear for rings sufficiently removed from the centre.

## 6. DISCUSSION AND CONCLUSION.

The similarity of the different observed facts in connection with the metal plates employed in the present case, with the metal-plate-colours obtained by heating, is quite apparent. The experiments in the present case however, could not be pushed further and all attempts for a quantitative study of the intensity of the scattered light and its verification according to the theory developed by the present author in the previous paper mentioned before, proved unsuccessful. The difficulty lies in the fact that the rings are so near together and the different colours are thus blended with one another that it is impossible to select a portion of moderate dimensions which would show uniform scattered colours due to the particles of similar dimensions. The method proved quite unsuitable for the present case and can only be used in cases where the entire metal surface is coloured uniformly giving the same tint. In spite of that, the complementary nature of the reflected and scattered light as shown by the photographs and the qualitative study of the reflected and scattered light at once suggest that the colour must be due to the granular deposition of particles liberated during electrolysis. As it is metallic copper which is deposited in case of copper sulphate solution, we get no colour except that of the metal itself. But in the other cases it is the oxide of the metal which is deposited and hence the root cause of the colours is identical with the case of heated metal surfaces.

(i) In the present paper an attempt has been made to explain the colours shown by Nobili's rings. All observed facts support the view that the colours must be due to the diffraction of light by the granular structure formed during electrolysis.

(ii) Photographs are given showing the complementary nature of the reflected and scattered light which fact supports the idea of Diffraction as the origin of the Colours.

The best thanks of the author are due to Prof. C. V. Raman who suggested this work.

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# Prevision of Earthquakes

BY

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It has been pointed out by Davison <sup>1</sup> that, though a prediction of earthquakes is not possible, we may attempt at their prevision, prediction being an accurate form of forecast, while prevision is only an approximate form of it. Dr. Davison has referred to two methods of prevision, both of them being applicable to the earthquakes of tectonic origin. One of them is due to Prof. Reid <sup>2</sup> and consists in erecting "a line of piers, say a kilometer apart, at right angles to the direction which a geological examination of the region, or past experience indicates the fault will take when the rupture occurs; and a careful determination, from time to time, of the directions of the lines joining successive piers, their differences of level, and the exact distance between them, would reveal any strains which might be developing along the region the line of piers crosses." The second method which we owe to Dr. Davison himself consists in carefully recording the fore-shocks and the after-shocks and depends on the hypothesis that "the increase in seismic activity along a known fault, and the tendency of uniformity in the distribution of that activity along the fault, may be heralds of the great crust-movements which cause disastrous earthquakes."<sup>3</sup> It is clear that Davison's method of prevision depends entirely on a careful recording of the fore-shocks and the after-shocks.

<sup>1</sup> Science Progress, Vol. IX, pp. 639-645, 1914-1915.

<sup>2</sup> Reid, The California Earthquake of April 18, 1906, Report of the State Earthquake Investigation Commission, Vol. II, p. 131, 1910.

<sup>3</sup> *Loc. cit.*, p. 645.

The Indian seismic tract No. 8 of Count F. de Montessus de Ballore comprising the Eastern Himalayas, Assam and Lower Bengal must have experienced a large number of shocks in the past as shown by the big shocks of (i) the 10th January, 1869, (ii) the 14th July, 1885, (iii) the 12th June, 1897 and (iv) the 8th July, 1918, but any systematic recording of the earthquake shocks was, evidently, seriously undertaken only after the great earthquake of 1897. The following figures have been published regarding the number of shocks recorded at Shillong<sup>1</sup> :—

Year	No. of shocks.
1897 (Aug.-Dec.)	444
1898	486
1899	246
1900	193
1901	164
1902	135
1903-1908	No figures available.
1909-1913	16
1914-1917	114

These figures clearly show the evidence of renewed seismic activity during 1914-1917 which began during 1909-1913 and these shocks were but the fore-shocks or the fore-runners of the Srimangal earthquake of 1918. This earthquake originated in the seismic tract No. 8 and furnishes an evidence supporting Dr. Davison's method of earthquake prevision.

While dealing with the question of the prevision of the earthquakes in India all of which are of a tectonic origin, attention may be drawn to one important consideration. In the tectonic quakes the transfer of load from one part and its re-deposition in another part in such a way that a considerable amount of strain is set up along lines of comparative instability are the chief originating factors. So far as the

<sup>1</sup> These figures have been obtained from (i) Mem. Geol. Surv. India, Vol. 30 pp. 1-102, 1900, (ii) Mem. Geol. Surv. Ind., Vol. 35, pp. 117-150, 1903, and (iii) Proc Asiatic Soc., Bengal, Vol. XIV, pp. xxii-xxiii, 1918.

Indian earthquakes are concerned the redistribution is carried on chiefly by running water, the transporting power being dependent upon various factors including its own volume. The amount of the available running water will depend primarily upon the amount of the rainfall and snowfall, while with an increase in the number of wet days, there is the chance of a decrease in the amount that may be lost by evaporation. The denudation work in an arid land is different from what prevails in a moist one and, on the Indian side of the Himalaya Mountains, in the work of denudation the most prominent part is played by rain and snow. It is, accordingly, not unlikely that in a country of tectonic earthquake, where the main work of denudation is carried on by the running water, there may be some sort of cause and effect relationship between the amount of rainfall and earthquake periodicity. In other words, it is not impossible that in such a country, after a number of years, the transfer and re-deposition of the load may be in such a proportion that a great strain is produced resulting in an earthquake due to the formation of a fault. A little consideration, however, shows that the question is not really so simple as it appears to be. Thus, for example, in the case of earthquakes of this nature it is quite likely that in the same tract the amount of the removed material need not always be approximately of the same load in all big earthquakes of tectonic origin. When the isostasy has been once established after the occurrence of a big earthquake, the crustal condition has certainly undergone some changes and, for the causation of the next earthquake, it is quite possible that the load, the redistribution of which may give rise to the shock, may be of a magnitude quite different from what was the origin of the preceding shock and eventually a time will come when the factors contributing towards the isostatic disturbance will disappear and there will be no earthquake. This mode of prevision is merely

a suggestion, but I think that it is worth testing. The idea is not a new one for I find that the late Prof. Knott was also inclined to believe in the same way <sup>1</sup> and the late Prof. Omori pointed out that in the whole of the Meiji area in Japan there was a remarkable coincidence between the frequency of the earthquakes and the amount of rain and snowfall.<sup>2</sup>

The tract No. 8 of Count F. de Montessus de Ballore is the most unstable portion of India and is also characterised by an abundance of rainfall. For a critical examination of the hypothesis outlined above, the seismic activity and the amount of rainfall of this region should be compared, but unfortunately from the incomplete earthquake and rainfall data nothing definite can be established at present regarding this relationship, but if careful observations are commenced now, and continued for some length of time, then we may arrive at some definite result.<sup>3</sup> It appears that each of the big shocks experienced in this area since 1869 occurred after a big interval during which disturbance of the isostatic condition was possible and in this disturbance, the denudation, transportation and deposition of the materials had certainly some share and they depended chiefly on the amount of rainfall. This hypothesis is, however, tenable only on the assumption that the earthquakes originate at a small distance from the surface of the earth.<sup>4</sup>

<sup>1</sup> Physics of earthquake phenomena (1908), p. 129.

<sup>2</sup> Nature, March 20, 1913, p. 65.

<sup>3</sup> Though a list of earthquakes was prepared and published by the late Dr. Oldhan (Mem. Geol. Surv. Ind., Vol. XIX, pp. 163-215) dating from 893 or 894 A.D. no reliance can be put on the shocks chronicled as the data are extremely incomplete. Between the chronicled first and second shocks there is a gap of a little over 600 years.

<sup>4</sup> There seems to be at present a considerable difference of opinion regarding this point. Mr. Walker (Phil. Tran. Roy. Soc. Ser. A, Vol. 222, pp. 45-56, 1921) put the focus of an earthquake shock as low as 1250 km. though his results have been challenged by Dr. Banerjee (Nature, Jan. 26, p. 108, 1922). In a paper read before the Geological Society of London (Q. J. G. S. pp. 231-236, 1923.) Mr. R. D. Oldham has come to the conclusion that the ultimate origin of the earthquake of the 7th August, 1895, in Northern Italy, must have been of the order of 100 miles or more.

# On the Motion Generated in a Viscous Liquid by the Translation of Certain Quartic Cylinders.

BY

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## INTRODUCTION.

1. It was first pointed out by Sir G. Stokes<sup>1</sup> that the two-dimensional motion of a circular cylinder with uniform velocity is impossible, when the equations of motion are simplified by the neglect of the "inertia terms." The explanation given by him suggests that the problem is insoluble for a cylinder of any form, if the "inertia terms" are neglected.

In a recent paper,<sup>2</sup> published in the proceedings of the Royal Society, an imperfect solution of the problem, when the moving body is an elliptic cylinder is given. Here the inertia terms are neglected, the condition of no tangential slipping at the surface is satisfied, but the velocity at infinity in one direction is infinite, which is contrary to experience.

In the present paper I have investigated the motion of cylinders whose cross-sections are

- (i) the inverse of an ellipse, and
- (ii) the elliptic limacon.

<sup>1</sup> Stokes, 'Mathematical and Physical Papers,' Vol. 3, p. 65.

<sup>2</sup> A. Berry and Miss L. M. Swain—'On the Steady Motion of a Cylinder through Infinite Viscous Fluid,' Proc. Roy. Soc., Series A, Vol. 102, No. 719, p. 766.

It is seen that the condition of no slipping is satisfied at the surface exactly; the velocity vanishes at infinity; it is everywhere finite and continuous and last of all a definite value for the resistance is obtained.

The motion of the cylinder whose cross-section is an elliptic limacon, parallel to the axis of  $y$  (*i.e.*, in a direction perpendicular to the line of foci) presents difficulties with regard to continuity of motion along the double lines  $\eta=0$ . The treatment of this case is reserved for a subsequent communication.

## SECTION I.

### THE INVERSE OF AN ELLIPSE.

#### 2. *The Transformation.*

Let

$$x+iy=c \sec (\xi+i\eta).$$

Then

$$c./r^2=\cosh \eta \cos \xi.$$

$$cy/r^2=\sinh \eta \sin \xi.$$

$$2c^2/r^2=\cosh 2\eta+\cos 2\xi.$$

and

$$h^2=\left(\frac{d\xi}{dx}\right)^2+\left(\frac{d\xi}{dy}\right)^2.$$

$$=\left(\frac{d\eta}{dx}\right)^2+\left(\frac{d\eta}{dy}\right)^2.$$

$$\equiv (\cosh 2\eta + \cos 2\xi)^2 / 2c^2 (\cosh 2\eta - \cos 2\xi).$$

The curves  $\xi=\alpha$  and  $\eta=\beta$  are the inverse of a family of confocal hyperbolæ and ellipses.

### 3. *The Stream-Function.*

When the inertia terms are neglected, the stream-function  $\psi$  for two-dimensional motion satisfies the equation

$$\nabla^4 \psi = 0.$$

where  $\nabla^2$  has the usual meaning.

To find a solution, let us write

$$\begin{aligned} \psi &\equiv H_1 \sin \xi + H_2 \sin \xi / (\cosh 2\eta + \cos 2\xi), \\ &= \psi_1 + \psi_2 \end{aligned}$$

where  $H_1$  and  $H_2$  are functions of  $\eta$  alone.

Then

$$2c^2 \nabla^2 \psi_1 = (H_1'' - H_1) \frac{(\cosh 2\eta + \cos 2\xi)^2}{(\cosh 2\eta - \cos 2\xi)} \sin \xi.$$

Operating on both sides by  $\delta^2$  which stands for

$$\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2},$$

we have

$$\begin{aligned} 2c^2 \delta^2 \nabla^2 \psi_1 &= \frac{\sin \xi}{(\cosh 2\eta - \cos 2\xi)^2} [(4P - P'') \cos^2 2\xi \\ &\quad - (P' \cosh 2\eta + 12P' \sinh 2\eta + 20P \cosh 2\eta) \cos^2 2\xi \\ &\quad + \{(P'' - 4P) \cosh^2 2\eta + 16P - 8 \sinh 2\eta \times \\ &\quad (P' \cosh 2\eta + 2P \sinh 2\eta)\} \cos 2\xi + (P'' \cosh 2\eta \\ &\quad + 4P' \sinh 2\eta + 4P \cosh 2\eta) \cosh^2 2\eta + 32P \cosh 2\eta \\ &\quad - P (\cosh 2\eta + \cos 2\xi)^2 (\cosh 2\eta - \cos 2\xi) \\ &\quad - 4P (1 + \cos 2\xi) (\cosh 2\eta + \cos 2\xi) (3 \cosh 2\eta - \cos 2\xi)] \end{aligned}$$

where  $P$  is written for  $H_1'' - H_1$ .



Similarly

$$2c^2 \nabla^2 \psi_1 = \frac{\sin \xi}{(\cosh 2\eta - \cos 2\xi)} [H''_1 (\cosh 2\eta + \cos 2\xi)$$

$$-4H'_1 \sinh 2\eta + H_1 (3 \cosh 2\eta + 1 - \cos 2\xi)].$$

therefore

$$2c^2 \delta^2 \nabla^2 \psi_1 = \frac{\sin \xi}{(\cosh 2\eta - \cos 2\xi)} [H''_1 (\cosh^2 2\eta - \cos^2 2\xi)$$

$$-8H_1''' \sinh 2\eta \cos 2\xi + 16H_1'' - 8H_1'' \cosh 2\eta (1 + \cos 2\xi)$$

$$-H_1'' (\cosh^2 2\eta - \cos^2 2\xi) - 4H_1''' \sinh 2\eta - (\cosh 2\eta - \cos 2\xi)$$

$$-16H_1'' (1 - \cosh 2\eta \cos 2\xi) + 16H_1' \sinh 2\eta (1 + \cos 2\xi)$$

$$+ 4H_1' \sinh 2\eta (\cosh 2\eta - \cos 2\xi) + 3(H_1'' - H_1) (\cosh 2\eta - \cos 2\xi)^2$$

$$+ 2H_1'' (1 + \cos 2\xi) (\cosh 2\eta - \cos 2\xi) - 8H_1' \sinh 2\eta (1 + \cos 2\xi)$$

$$-8H_1 (\cosh 2\eta \cos 2\xi - 1) - 2H_1 (1 + \cos 2\xi) (\cosh 2\eta - \cos 2\xi)$$

$$+ 2H_1'' (\cosh 2\eta - \cos 2\xi) - 8H_1' \sinh 2\eta$$

$$+ 8H_1 (\cosh 2\eta + \cos 2\xi) - 8H_1 (1 + \cos 2\xi)$$

$$- 2H_1 (\cosh 2\eta - \cos 2\xi)].$$

Adding  $\delta^2 \nabla^2 \psi_1$  and  $\delta^2 \nabla^2 \psi_2$  and equating to zero the co-efficients of the several powers of  $\cos 2\xi$ , we are led to the following equations.

$$P'' - 9P = 0 \quad \dots (1)$$

$$(P'' \cosh 2\eta + 12P' \sinh 2\eta + 20P \cosh 2\eta) - P \cosh 2\eta$$

$$+ 4P(2 \cosh 2\eta - 1) + H_1' - 2H_1'' + H_1 = 0. \quad \dots (2)$$

$$\{(P'' - 4P) \cosh^2 2\eta + 16P - 8 \sinh 2\eta (P' \cosh 2\eta + 2P \sinh 2\eta)\}$$

$$- P \cosh^2 2\eta - 4P(3 \cosh^2 2\eta + 2 \cosh 2\eta) - 4H_1''' \sinh 2\eta$$

$$+ 4H_1'' \cosh 2\eta + 4H_1' \sinh 2\eta - 4H_1 \cosh 2\eta$$

$$- 4H_1'' + 4H_1 = 0. \quad \dots (3)$$

$$\begin{aligned}
& \cosh^2 2\eta (P'' \cosh 2\eta + 4P' \sinh 2\eta + 4P \cosh 2\eta) + 32P \cosh 2\eta \\
& - P \cosh^3 2\eta - 12P \cosh^2 2\eta + H_2'' \cosh^2 2\eta - 4H_2''' \sinh 2\eta \cosh 2\eta \\
& + 4H_2' \sinh 2\eta \cosh 2\eta + H_2'' (2 \cosh^2 2\eta - 4 \cosh 2\eta) \\
& + H_2 (4 \cosh 2\eta - 3 \cosh^2 2\eta) = 0. \quad \dots \quad (4)
\end{aligned}$$

Solving we get

$$P = A \cosh 3\eta + B \sinh 3\eta.$$

Therefore

$$\begin{aligned}
H_1 &= \frac{1}{8} (A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta. \\
H_2 &= -\frac{1}{16} (A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{16} (A \cosh 3\eta \\
&+ B \sinh 3\eta) + E \cosh \eta + F \sinh \eta + G \eta \cosh \eta + H \eta \sinh \eta.
\end{aligned}$$

Substituting in the two equations (3) and (4) we get

$$G = 0.$$

The stream-function can therefore be written in the form

$$\begin{aligned}
\psi &= \left\{ \frac{1}{8} (A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \right\} \sin \xi \\
&+ \left\{ -\frac{1}{16} (A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{16} (A \cosh 3\eta + B \sinh 3\eta) \right. \\
&\left. + E \cosh \eta + F \sinh \eta + H \eta \sinh \eta \right\} \left( \frac{\sin \xi}{(\cosh 2\eta + \cos 2\xi)} \right).
\end{aligned}$$

Let us suppose that the cylinder is moving along the axis of  $x$  with velocity  $U$  and that its cross-section is given by  $\eta = \beta$ .

If we write

$$u = -\frac{\partial \psi}{\partial y}, \quad v = \frac{\partial \psi}{\partial x}$$

then since at the boundary of the cylinder

$$u = U, \quad v = 0,$$

the boundary conditions are, when  $\eta = \beta$

$$\frac{\partial \psi}{\partial \xi} = -2cU \frac{\sinh \beta}{(\cosh 2\beta + \cos 2\xi)} \left\{ \cos \xi + \frac{2 \sin \xi \sin 2\xi}{(\cosh 2\beta + \cos 2\xi)} \right\}$$

$$\frac{\partial \psi}{\partial \eta} = -2cU \frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)} \left\{ \cosh \beta - \frac{2 \sinh \beta \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)} \right\} \quad (a)$$

But from the expression for the stream-function, we have, when  $\eta = \beta$

$$\begin{aligned} \frac{\partial \psi}{\partial \xi} = & \left\{ \frac{1}{8} (A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta \right. \\ & + D \sinh \beta \} \cos \xi + \left\{ -\frac{1}{16} (A \cosh 5\beta + B \sinh 5\beta) \right. \\ & + \frac{1}{16} (A \cosh 3\beta + B \sinh 3\beta) + E \cosh \beta + F \sinh \beta \\ & + H\beta \sinh \beta \} \left\{ \frac{\cos \xi}{(\cosh 2\beta + \cos 2\xi)} + \frac{2 \sin \xi \sin 2\xi}{(\cosh 2\beta + \cos 2\xi)^2} \right\} \\ \frac{\partial \psi}{\partial \eta} = & \left\{ \frac{3}{8} (A \sinh 3\beta + B \cosh 3\beta) + C \sinh \beta + D \cosh \beta \right\} \times \\ & \sin \xi + \left\{ -\frac{5}{16} (A \sinh 5\beta + B \cosh 5\beta) + \frac{3}{16} (A \sinh 3\beta \right. \\ & + B \cosh 3\beta) + E \sinh \beta + F \cosh \beta + H(\sinh \beta \\ & + \beta \cosh \beta) \} \frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)} - 2 \left\{ -\frac{1}{16} (A \cosh 5\beta + B \sinh 5\beta) \right. \\ & + \frac{1}{16} (A \cosh 3\beta + B \sinh 3\beta) + E \cosh \beta + F \sinh \beta + H\beta \sinh \beta \} \times \\ & \left. \frac{\sin \xi \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)^2} \right\} \quad (b) \end{aligned}$$

From (a) and (b) we are led to the following equations—

$$\frac{1}{8} (A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta = 0 \quad \dots (5)$$

$$\begin{aligned} & -\frac{1}{16} (A \cosh 5\beta + B \sinh 5\beta) + \frac{1}{16} (A \cosh 3\beta + B \sinh 3\beta) \\ & + E \cosh \beta + F \sinh \beta + H\beta \sinh \beta = -2cU \sinh \beta \quad \dots (6) \end{aligned}$$

$$\frac{3}{8} (A \sinh 3\beta + B \cosh 3\beta) + C \sinh \beta + D \cosh \beta = 0 \quad \dots (7)$$

$$\begin{aligned} & -\frac{5}{16} (A \sinh 5\beta + B \cosh 5\beta) + \frac{3}{16} (A \sinh 3\beta \\ & + B \cosh 3\beta) + E \sinh \beta + F \cosh \beta + H(\sinh \beta \\ & + \beta \cosh \beta) = -2cU \cosh \beta. \quad \dots (8) \end{aligned}$$

The orthogonal components of velocity are

$$-h \frac{\partial \psi}{\partial \xi} \quad \text{and} \quad h \frac{\partial \psi}{\partial \eta}.$$

At an infinite distance from the boundary,

$$\eta = \delta\eta \quad \text{and} \quad \xi = \frac{\pi}{2} - \delta\xi.$$

$$\cosh 2\eta + \cos 2\xi = 2(\delta\eta^2 + \delta\xi^2).$$

In order that

$$h \frac{\partial \psi}{\partial \xi}$$

may vanish at infinity, the expression

$$\begin{aligned} & \left\{ -\frac{1}{16}(A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{16}(A \cosh 3\eta + B \sinh 3\eta) \right. \\ & \left. + E \cosh \eta + F \sinh \eta + H\eta \sinh \eta \right\} \end{aligned}$$

must be of the second order of small quantities.

This requires that

$$E=0, \quad -\frac{1}{8}B + F=0. \quad \dots \quad (9)$$

In order that

$$h \frac{\partial \psi}{\partial \eta}$$

may vanish at infinity the numerator of the expression

$$\begin{aligned} & \frac{1}{2} \left\{ -\frac{1}{16}(A \sinh 5\eta + B \cosh 5\eta) + \frac{1}{16}(A \sinh 3\eta \right. \\ & \left. + B \cosh 3\eta) + E \sinh \eta + F \cosh \eta + H(\sinh \eta \right. \\ & \left. + \eta \cosh \eta) \right\} - \frac{\sinh 2\eta}{(\cosh 2\eta + \cos 2\xi)} \left\{ -\frac{1}{16}(A \cosh 5\eta \right. \\ & \left. + B \sinh 5\eta) + \frac{1}{16}(A \cosh 3\eta + B \sinh 3\eta) + E \cosh \eta \right. \\ & \left. + F \sinh \eta + H\eta \sinh \eta \right\} \end{aligned}$$

must be of the third order of small quantities.

We then get the equations

$$E=0, -\frac{1}{8}B+F=0;$$

which are identical with the equations obtained above in (9).

At a point near the foci,

$$\eta=\delta\eta, \xi=\delta\xi \text{ or } \pi-\delta\xi,$$

$$h=c^{-1}(\delta\eta^2+\delta\xi^2)^{-\frac{1}{2}}$$

$$\text{and } \cosh 2\eta + \cos 2\xi = 2.$$

In order that the velocity at this point may be finite, the expression

$$\begin{aligned} & \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \\ & + \frac{1}{2} \left\{ -\frac{1}{16}(A \cosh 5\eta + B \sinh 5\eta) + \frac{1}{16}(A \cosh 3\eta + B \sinh 3\eta) \right. \\ & \left. + E \cosh \eta + F \sinh \eta + H \eta \sinh \eta \right\} \end{aligned}$$

must be of the first order of small quantities.

This gives the additional equation

$$\frac{1}{8}A + C = 0. \quad \dots (10)$$

Solving the equations (5), (6), (7), (8), (9) and (10) we have

$$A = -8C = \frac{4cU}{\beta}.$$

$$B = 8F = -\frac{4cU}{\beta} \cosh 2\beta.$$

$$D = \frac{cU}{2\beta} \frac{(\cosh 2\beta + 2)}{(\cosh 2\beta - 1)} \tanh \beta.$$

$$H = -\frac{2cU}{\beta}$$

Whence we get the equation

$$A + 2H = 0 \quad \dots (11)$$

*The Continuity of Motion.*

4. If the motion is continuous along the double lines  $\eta=0$ , the derivatives of  $\psi$  will either vanish when  $\eta=0$ , or change sign in passing from one side to the other. Now from (b) it is seen that

$$\frac{\partial \psi}{\partial \xi} = 0$$

when we write  $\eta=0$  instead of  $\eta=\beta$  in (b), by virtue of the equations (9) and (10).

$\frac{\partial \psi}{\partial \eta}$  is easily seen to change sign when we write  $2\pi - \xi$  or  $-\xi$  for  $\xi$ .

Hence the motion is continuous along the line  $\eta=0$ , extending from the points  $(x = \pm c, y=0)$  to infinity. It can also be shown that the vorticity is finite everywhere. Further if  $u, v$  be the velocities parallel to the axes of  $x$  and  $y$  respectively, then it can be shown that the velocity-gradients, *viz.*,

$$\frac{\partial u}{\partial x}, \quad \frac{\partial v}{\partial y}$$

etc., are finite at all points.

*The Pressure.*

5. We know that  $\mu \nabla^2 \psi$  and  $p$  are conjugate functions.

$$\begin{aligned} \mu \nabla^2 \psi = \frac{\mu}{2c^2} & \left[ A \left\{ -\frac{1}{2} \sin 3\xi \cosh 3\eta - \frac{1}{2} \sin \xi \cosh \eta \right. \right. \\ & + \left. \frac{2 \sin \xi \cosh \eta}{(\cosh 2\eta - \cos 2\xi)} \right\} + B \left\{ -\frac{1}{2} \sin 3\xi \sinh 3\eta \right. \\ & \left. \left. - \frac{1}{2} \sin \xi \sinh \eta \right\} + H \left\{ -2 \sin \xi \cosh \eta + \frac{4 \sin \xi \cosh \eta}{(\cosh 2\eta - \cos 2\xi)} \right\} \right]. \end{aligned}$$

Making use of equation (11), we find

$$p = \frac{\mu}{2c^2} \left[ A \left\{ -\frac{1}{2} \cos 3\xi \sinh 3\eta - \frac{3}{2} \cos \xi \sinh \eta \right\} \right. \\ \left. + B \left\{ -\frac{1}{2} \cos 3\xi \cosh \eta - \frac{3}{2} \cos \xi \cosh \eta \right\} \right. \\ \left. - 2H \cos \xi \sinh \eta \right] + \Pi_0.$$

where  $\Pi_0$  is the pressure at infinity.

It is at once clear that the pressure is finite everywhere.

### *The Resistance.*

6. The rates of elongation of the shear are given by

$$e = -f = \frac{1}{2} \left( \frac{\partial h^2}{\partial \xi} \frac{\partial \psi}{\partial \eta} + \frac{\partial h^2}{\partial \eta} \frac{\partial \psi}{\partial \xi} \right) + h^2 \frac{\partial^2 \psi}{\partial \xi \partial \eta} \\ *r = h^2 \left( \frac{\partial^2 \psi}{\partial \eta^2} - \frac{\partial^2 \psi}{\partial \xi^2} \right) + \frac{\partial h^2}{\partial \eta} \frac{\partial \psi}{\partial \eta} - \frac{\partial h^2}{\partial \xi} \frac{\partial \psi}{\partial \xi}.$$

when  $\eta = \beta$ .

$$2c^2 \frac{\partial h^2}{\partial \xi} = -2 \sin 2\xi (\cosh 2\beta + \cos 2\xi) \frac{(3 \cosh 2\beta - \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)^2} \\ 2c^2 \frac{\partial h^2}{\partial \eta} = 2 \sinh 2\beta (\cosh 2\beta + \cos 2\xi) \frac{(\cosh 2\beta - 3 \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)^2}.$$

$$\frac{\partial^2 \psi}{\partial \xi \partial \eta} = 2cU \sinh \beta \left\{ \frac{2 \cos \xi \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)^2} \right. \\ \left. + \frac{8 \sin \xi \sin 2\xi \sinh 2\beta}{(\cosh 2\beta + \cos 2\xi)^2} - (2cU \cosh \beta) \times \right. \\ \left. \left\{ \frac{\cos \xi}{(\cosh 2\beta + \cos 2\xi)} + \frac{2 \sin \xi \sin 2\xi}{(\cosh 2\beta + \cos 2\xi)^2} \right\} \right\}.$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = -2cU \sinh \beta \left\{ -\frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)} + 4 \frac{\sin 3\xi}{(\cosh 2\beta + \cos 2\xi)^2} \right.$$

$$\left. + 8 \frac{\sin \xi \sin^2 2\xi}{(\cosh 2\beta + \cos 2\xi)^3} \right\}.$$

$$\frac{\partial^2 \psi}{\partial \eta^2} = L(\beta) \sin \xi + M(\beta) \frac{\sin \xi}{(\cosh 2\beta + \cos 2\xi)}$$

$$+ 8cU \frac{\sinh 3\beta \sin \xi}{(\cosh 2\beta + \cos 2\xi)^2} - 16cU \frac{\sinh \beta \sinh^2 2\beta \sin \xi}{(\cosh 2\beta + \cos 2\xi)^3}.$$

where

$$L(\beta) = \frac{2}{3}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta.$$

$$M(\beta) = -\frac{25}{16} \left( A \cosh 5\beta + B \sinh 5\beta \right)$$

$$+ \frac{9}{16} \left( A \cosh 3\beta + B \sinh 3\beta \right) + F \sinh \beta$$

$$+ H(2 \cosh \beta + \beta \sinh \beta)$$

and

$$\frac{\partial \psi}{\partial \xi}, \quad \frac{\partial \psi}{\partial \eta}$$

are given by (a).

substituting we find  $e=f=0$ .

$$\gamma = \left[ \frac{L(\beta)}{2c^2} \frac{(\cosh 2\beta + \cos 2\xi)^2}{(\cosh 2\beta - \cos 2\xi)} \sin \xi \right.$$

$$+ \frac{M(\beta)}{2c^2} \frac{(\cosh 2\beta + \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)} \sin \xi - 8 \frac{U}{c} \frac{\sinh \beta \sin \xi}{(\cosh 2\beta - \cos 2\xi)}$$

$$+ 4 \frac{U}{c} \frac{(\sinh 3\beta \sin \xi + \sinh \beta \sin 3\xi)}{(\cosh 2\beta - \cos 2\xi)}$$

$$\left. - 7 \frac{U}{c} \frac{\sinh \beta (\cosh 2\beta + \cos 2\xi)}{(\cosh 2\beta - \cos 2\xi)} \sin \xi \right].$$



The resistance on the cylinder is given by

$$R = \int \left( P \frac{dy}{ds} - W \frac{dx}{ds} \right) ds$$

where  $W = \mu\gamma$ , and the integration being taken round the boundary of the curve.

Integrating,

$$\begin{aligned} R = & -\pi \frac{\mu}{c} \cosh \beta \left\{ L(\beta) + M(\beta) + 2cU \sinh \beta \right\} \\ & - 2\pi \frac{\mu}{c} \sinh \beta \left\{ \frac{3}{4} \left( A \sinh 3\beta + B \cosh 3\beta \right) \right. \\ & \left. + \frac{3}{4} \left( A \sinh 5\beta + B \cosh 5\beta \right) - H \sinh \beta \right\}. \\ & = 4\pi\mu U, \beta, \end{aligned}$$

or restoring the values of the constants.

It is remarkable that the resistance is independent of  $c$ .

The motion parallel to the axis of  $y$  can be obtained in an exactly similar manner.

## SECTION II.

### ELLIPTIC LIMAÇON.

7.

*The transformation.*

If

$$\xi + i\eta = 2 \sec^{-1} \sqrt{\frac{1 + iy}{2c}},$$

then

$$4cx/r^2 = 1 + \cosh \eta \cos \xi,$$

$$4cy/r^2 = \sinh \eta \sin \xi.$$

$$r = 4c/(\cosh \eta + \cos 2\xi).$$

and

$$h^2 = \frac{1}{16c^2} \frac{(\cosh \eta + \cos \xi)^2}{(\cosh \eta - \cos \xi)^2}.$$

The curves  $\eta = \text{constant}$  are elliptic limaçons, while the curves  $\xi = \text{constant}$  are hyperbolic limaçons.

### 8. *The Current-function.*

To investigate the motion parallel to the axis of  $x$  (i.e., the line joining the foci), let us assume

$$\begin{aligned} \psi &= H_1 \sin \xi + H_2 \frac{\sin \xi}{(\cosh \eta + \cos \xi)} + H_3 \frac{\sin \xi}{(\cosh \eta + \cos \xi)^2}, \\ &= \psi_1 + \psi_2 + \psi_3. \end{aligned}$$

where  $H_1$ ,  $H_2$  and  $H_3$  are functions of  $\eta$  alone.

Then

$$16c^2 \nabla^2 \psi_1 = \sin \xi \frac{(\cosh \eta + \cos \xi)^2}{(\cosh \eta - \cos \xi)^2} (H_1'' - H_1).$$

Operating as before by  $\delta^2$ , we have

$$\begin{aligned} 16c^2 \delta^2 \nabla^2 \psi_1 &= \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2} \left[ (\cosh \eta + \cos \xi)^2 \times \right. \\ &\quad \cdot \{ 2(\cosh 2\eta + \cos 2\xi - 8 \cosh \eta \cos \xi + 8) P \\ &\quad + 4 \sinh \eta (\cosh \eta - 2 \cos \xi) P' + (\cosh^2 \eta - \cos^2 \xi) P'' \\ &\quad \left. - 4(2 \cosh \eta - \cos \xi) \cos \xi P - (\cosh^2 \eta - \cos^2 \xi) P \} \right]. \end{aligned}$$

where

$$P = H_1'' - H_1.$$

similarly

$$\begin{aligned} 16c^2 \nabla^2 \psi_2 &= \frac{\sin \xi}{(\cosh \eta - \cos \xi)} \left[ (\cosh \eta + \cos \xi)^2 H_2'' \right. \\ &\quad \left. - 2 \sinh \eta (\cosh \eta + \cos \xi) H_2' \right] \end{aligned}$$

Therefore

$$\begin{aligned}
 16c^2 \delta^2 \nabla^2 \psi_s = & \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2} \left[ (\cosh^2 \eta - \cos^2 \xi) \times \right. \\
 & \{ (\cosh \eta + \cos \xi) H_s^{(4)} + 2 \sinh \eta H_s^{(3)} + (\cosh \eta - \cos \xi) H_s^{(2)} \} \\
 & + 4(\cosh \eta + \cos \xi) H_s^{(2)} - 4 \sinh \eta \cos \xi \{ (\cosh \eta + \cos \xi) H_s^{(3)} \\
 & + \sinh \eta H_s^{(2)} \} + 4 \cosh \eta (1 - \cos^2 \xi) H_s^{(2)} \\
 & - 2 \sinh \eta \{ (\cosh^2 \eta - \cos^2 \xi) H_s^{(3)} - 4 \sinh \eta \cos \xi H_s^{(2)} \} \\
 & - 8 \sinh \eta H_s^{(2)} - 4 \cosh \eta \{ (\cosh^2 \eta - \cos^2 \xi) H_s^{(2)} \\
 & - 2 \sinh \eta \cos \xi H_s^{(2)} \} - 2 \sinh \eta' \cosh^2 \eta - \cos^2 \xi) H_s^{(2)} \\
 & - 2(\cosh \eta + \cos \xi)(3 \cosh \eta - \cos \xi) \cos \xi H_s^{(2)} \\
 & + 8 \sinh \eta \cosh \eta \cos \xi H_s^{(2)} - (\cosh \eta + \cos \xi)^2 (\cosh \eta - \cos \xi) H_s^{(2)} \\
 & \left. + 2 \sinh \eta (\cosh^2 \eta - \cos^2 \xi) H_s^{(2)} \right]
 \end{aligned}$$

Also

$$\begin{aligned}
 16c^2 \nabla^2 \psi_s = & \frac{\sin \xi}{(\cosh \eta - \cos \xi)} \left[ \{ (\cosh \eta + \cos \xi) H_s^{(2)} \right. \\
 & - 4 \sinh \eta H_s^{(2)} + 4(\cosh \eta - \cos \xi) H_s^{(2)} + 4 \cos \xi H_s^{(2)} \\
 & \left. - (\cosh \eta - \cos \xi) H_s^{(2)} \} \right].
 \end{aligned}$$

Therefore

$$\begin{aligned}
 16c^2 \delta^2 \nabla^2 \psi_s = & \frac{\sin \xi}{(\cosh \eta - \cos \xi)^2} \left[ (\cosh^2 \eta - \cos^2 \xi) H_s^{(4)} \right. \\
 & - 4 \sinh \eta - \cos \xi H_s^{(3)} + 4 H_s^{(3)} - 4 \sinh \eta (\cosh \eta - \cos \xi) H_s^{(3)} \\
 & - 8(1 - \cosh \eta \cos \xi) H_s^{(2)} + 4(\cosh \eta - \cos \xi)^2 H_s^{(2)} \\
 & + 8 \sinh \eta \cos \xi H_s^{(2)} - 4 \cosh \eta \cos \xi H_s^{(2)} \\
 & - 4(\cosh \eta - \cos \xi)^2 H_s^{(2)} + 4 \sinh \eta \cosh \eta - \cos \xi) H_s^{(2)} \\
 & - (\cosh^2 \eta - \cos^2 \xi) H_s^{(2)} + 4(\cosh \eta - \cos \xi) \cos \xi (H_s^{(2)} - H_s^{(2)}) \\
 & - 8 \sinh \eta \cos \xi H_s^{(2)} + 8(1 - \cosh \eta \cos \xi) H_s^{(2)} \\
 & - (\cosh^2 \eta - \cos^2 \xi) H_s^{(2)} + 4 \sinh \eta \cos \xi H_s^{(2)} \\
 & \left. - 4 H_s^{(2)} + 4 \cosh \eta \cos \xi H_s^{(2)} + (\cosh^2 \eta - \cos^2 \xi) H_s^{(2)} \right].
 \end{aligned}$$

Adding

$$\delta^2 \nabla^2 \psi_1, \quad \delta^2 \nabla^2 \psi_2 \quad \text{and} \quad \delta^2 \nabla^2 \psi_3$$

and equating to zero the co-efficients of the several powers of  $\cos \xi$ , we obtain the following equations

$$P'' - 9P = 0 \quad \dots \quad (12)$$

$$6 \cosh \eta P + 8 \sinh \eta P' + 2 \cosh \eta P'' + H_2{}^{\prime\prime} - 4H_2{}^{\prime\prime\prime} = 0 \quad \dots \quad (13)$$

$$\begin{aligned} (2 \cosh 2\eta + 14)P + 4 \sinh \eta \cosh \eta P' - 8 \cosh \eta \times (16 \cosh \eta P + 8 \sinh \eta P' \\ - 8 \cosh^2 \eta P - \cosh \eta H_2{}^{\prime\prime} - 4 \sinh \eta H_2{}^{\prime\prime\prime} + \cosh \eta H_2{}^{\prime\prime\prime\prime} \\ - H_2{}^{\prime\prime}{}^{\prime\prime} + 2H_2{}^{\prime\prime\prime} - H_2 = 0 \end{aligned} \quad \dots \quad (14)$$

$$\begin{aligned} 2 \cosh \eta \{ (2 \cosh 2\eta + 14)P + \cosh^2 \eta P'' \} - 26 \cosh^3 \eta P \\ + \cosh^2 \eta H_2{}^{\prime\prime} - 4 \cosh^2 \eta H_2{}^{\prime\prime\prime} - 4 \sinh \eta \cosh \eta H_2{}^{\prime\prime\prime\prime} \\ + 16 \sinh \eta \cosh \eta H_2{}^{\prime} = 0 \end{aligned} \quad \dots \quad (15)$$

$$\begin{aligned} \cosh^2 \eta \{ (2 \cosh 2\eta + 14)P + 4 \sinh \eta \cosh \eta P' + \cosh^2 \eta P'' \} \\ - \cosh^4 \eta P + \cosh^3 \eta H_2{}^{\prime\prime} + 8 \cosh \eta H_2{}^{\prime\prime\prime} - 8 \sinh \eta H_2{}^{\prime} \\ - 4 \cosh^3 \eta H_2{}^{\prime\prime} + \cosh^2 \eta H_2{}^{\prime\prime}{}^{\prime\prime} - 4H_2{}^{\prime\prime}{}^{\prime\prime} - 4 \sinh \eta \cosh \eta H_2{}^{\prime\prime\prime\prime} \\ + 2 \cosh^2 \eta H_2{}^{\prime\prime} - 3 \cosh^2 \eta H_2 + 4 \sinh \eta \cosh \eta H_2{}^{\prime} + 4H_2 = 0 \end{aligned} \quad \dots \quad (16)$$

solving the equations we get,

$$P = A \cosh 3\eta + B \sinh 3\eta.$$

Therefore

$$H_1 = \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta$$

$$\begin{aligned} H_2 = -\frac{1}{8}(A \cosh 4\eta + B \sinh 4\eta) + E \cosh 2\eta \\ + F \sinh 2\eta + G\eta + H. \end{aligned}$$

$$\begin{aligned} H_3 = \frac{1}{32}(A \cosh 5\eta + B \sinh 5\eta) - \frac{1}{32}(A \cosh 3\eta \\ + B \sinh 3\eta) - \frac{1}{8}(E \cosh 3\eta + F \sinh 3\eta) \\ + I \cosh \eta + J \sinh \eta + K\eta \cosh \eta + L\eta \sinh \eta \end{aligned}$$

substituting in the equations (15) and (16) we obtain

$$\left. \begin{array}{l} G=0 \\ K=0 \end{array} \right\} \quad (17)$$

Therefore

$$\begin{aligned} \psi = & \left\{ \frac{1}{8}(A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta \right. \\ & + D \sinh \eta \} \sin \xi + \left\{ -\frac{1}{8}(A \cosh 4\eta + B \sinh 4\eta) \right. \\ & + E \cosh 2\eta + F \sinh 2\eta + H \} \frac{\sin \xi}{(\cosh \eta + \cos \xi)} \\ & + \left\{ \frac{1}{8}(A \cosh 5\eta + B \sinh 5\eta - A \cosh 3\eta - B \sinh 3\eta) \right. \\ & - \frac{1}{2}(E \cosh 3\eta + F \sinh 3\eta) + I \cosh \eta + J \sinh \eta \\ & \left. + L\eta \sinh \eta \right\} \frac{\sin \xi}{(\cosh \eta + \cos \xi)^2} \end{aligned}$$

Let the cross-section of the cylinder be denoted by  $\eta = \beta$  and suppose that it is moving with velocity  $U$  parallel to the axis of  $x$ .

The boundary conditions are when  $\eta = \beta$

$$\frac{\partial \psi}{\partial \xi} = -4cU \sinh \beta \left[ \frac{\cos \xi}{(\cosh \beta + \cos \xi)^2} + \frac{2 \sin^2 \xi}{(\cosh \beta + \cos \xi)^3} \right]$$

$$\frac{\partial \psi}{\partial \eta} = -4cU \sin \xi \left[ \frac{\cosh \beta}{(\cosh \beta + \cos \xi)^2} - \frac{2 \sinh^2 \beta}{(\cosh \beta + \cos \xi)^3} \right]$$

because  $u = U$  and  $v = 0$  at the boundary.

We then obtain the following equations (C)

$$\frac{1}{8}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta = 0 \quad \dots \quad (18)$$

$$-\frac{1}{8}(A \cosh 4\beta + B \sinh 4\beta) + E \cosh 2\beta + F \sinh 2\beta + H = 0 \quad \dots \quad (19)$$

$$\begin{aligned} & \frac{1}{8}(A \cosh 5\beta + B \sinh 5\beta - A \cosh 3\beta - B \sinh 3\beta) \\ & - \frac{1}{2}(E \cosh 3\beta + F \sinh 3\beta) + I \cosh \beta + J \sinh \beta \\ & + L\beta \sinh \beta = -4cU \sinh \beta \quad \dots \quad (20) \end{aligned}$$

$$\frac{1}{3}(A \sinh 3\beta + B \cosh 3\beta) + C \sinh \beta + D \cosh \beta = 0 \quad \dots (21)$$

$$-\frac{1}{3}(A \sinh 4\beta + B \cosh 4\beta) + 2E \sinh 2\beta + 2F \cosh 2\beta = 0 \quad \dots (22)$$

$$\begin{aligned} & \frac{1}{12}(A \sinh 5\beta + B \cosh 5\beta) - \frac{1}{32}(A \sinh 3\beta \\ & + B \cosh 3\beta) - \frac{1}{2}(E \sinh 3\beta + F \cosh 3\beta) \\ & + I \sinh \beta + J \cosh \beta + L(\sinh \beta + \beta \cosh \beta) = -4cU \cosh \beta \end{aligned} \quad (23)$$

At a point near infinity

$$\eta = \delta\eta, \quad \xi = \pi - \delta\xi$$

$$\cosh \eta - \cos \xi = 2$$

$$h = (16c)^{-1} (\delta\eta^2 + \delta\xi^2)^{3/2}$$

In order that  $h \frac{\partial \psi}{\partial \xi}$  may vanish at infinity, the expression

$$\begin{aligned} & \frac{1}{32}\{(A \cosh 5\eta + B \sinh 5\eta) - (A \cosh 3\eta + B \sinh 3\eta)\} \\ & - \frac{1}{2}(E \cosh 3\eta + F \sinh 3\eta) + I \cosh \eta + J \sinh \eta + L\eta \sinh \eta \end{aligned}$$

must be of the second order of small quantities. This gives the equations

$$\left. \begin{aligned} -\frac{1}{3}E + I &= 0 \\ \frac{1}{12}B - \frac{1}{2}F + J &= 0 \end{aligned} \right\} \quad \dots (24)$$

In order that  $h \frac{\partial \psi}{\partial \eta}$  may vanish at infinity, the expression

$$\begin{aligned} & (\cosh \eta + \cos \xi) \left\{ \frac{1}{32}(A \sinh 5\eta + B \cosh 5\eta) \right. \\ & - \frac{1}{32}(A \sinh 3\eta + B \cosh 3\eta) - \frac{1}{2}(E \sinh 3\eta \\ & + F \cosh 3\eta) + I \sinh \eta + J \cosh \eta + L(\sinh \eta \\ & + \eta \cosh \eta) \left. \right\} - 2 \sinh \eta \left\{ \frac{1}{32}(A \cosh 5\eta + B \sinh 5\eta) \right. \\ & - \frac{1}{32}(A \cosh 3\eta + B \sinh 3\eta) - \frac{1}{2}(E \cosh 3\eta \\ & + F \sinh 3\eta) + I \cosh \eta + J \sinh \eta + L\eta \sinh \eta \left. \right\} \end{aligned}$$

must be of the third order of small quantities.

This gives the additional equations

$$\left. \begin{aligned} -\frac{1}{4}E + I &= 0 \\ \frac{1}{16}B - \frac{3}{2}F + J &= 0 \end{aligned} \right\} \dots (25)$$

which are identical with the equations (24)

At a point near the external focus,

$$\eta = \delta\eta, \quad \xi = \delta\xi$$

$$\cosh \eta + \cos \xi = 2$$

and

$$h = c^{-1} (\delta\eta^2 + \delta\xi^2)^{-1/2}$$

In order that the velocity may be finite at this point, the expression

$$\begin{aligned} & \left\{ \frac{1}{8} (A \cosh 3\eta + B \sinh 3\eta) + C \cosh \eta + D \sinh \eta \right\} \\ & + \frac{1}{2} \left\{ -\frac{1}{8} A \cosh 4\eta + B \sinh 4\eta \right\} + (E \cosh 2\eta \\ & + F \sinh 2\eta + H) + \frac{1}{2} \left\{ \frac{1}{8} (A \cosh 5\eta + B \sinh 5\eta \right. \\ & - A \cosh 3\eta - B \sinh 3\eta) - \frac{1}{2} (E \cosh 3\eta + F \sinh 3\eta) \\ & \left. + I \cosh \eta + J \sinh \eta + L \eta \sinh \eta \right\} \end{aligned}$$

must be of the first order of small quantities.

This gives the equation

$$\frac{1}{16}A + C + \frac{1}{2}E + \frac{1}{2}H = 0 \dots (26)$$

where we have taken into account the equation (24).

We have not yet obtained sufficient number of equations to determine all the un-known constants. In fact we have obtained nine equations, viz., (18), (19), (20), (21), (22), (23), (24) and (26) but there are ten un-known constants in the expression for  $\psi$ . The remaining equation follows from the continuity of motion.

It is easily seen that  $\frac{\partial \psi}{\partial \eta}$  changes sign in passing from one side of the double lines  $\eta=0$  to the other. Hence it is continuous along the line  $\eta=0$ .

But  $\frac{\partial \psi}{\partial \xi}$  does not change sign when we write  $-\xi$  for  $\xi$ . Hence in order that the motion may be continuous,  $\frac{\partial \psi}{\partial \xi}$  must be zero at  $\eta=0$ .

This gives the two additional equations

$$\left. \begin{aligned} \frac{1}{3}A + C &= 0 \\ -\frac{1}{3}A + E + H &= 0 \end{aligned} \right\} \quad \dots \quad (27)$$

From these two equations the equation (26) follows at once.

Thus we get ten equations to determine the ten un-known constants.

Solving, we have

$$A = -8C = 8H = (4cU/S) \sinh 2\beta$$

$$B = (-4cU/S) \cosh 2\beta$$

$$D = (cU/2S)(\cosh 2\beta + 2)$$

$$E = I = 0$$

$$F = (-cU/S)$$

$$J = (cU/4S)(\cosh 2\beta - 6)$$

$$L = (-cU/S) \sinh 2\beta$$

and 
$$S = \frac{1}{4}\{\beta \sinh 2\beta - (\cosh 2\beta - 1)\}$$

It is easily seen that

$$A + 4L = 0 \quad \dots \quad (28)$$

It may be remarked that the vorticity and velocity-gradients are finite everywhere.



*The Pressure.*

9. Since  $\mu \nabla^2 \psi$  and  $p$  are conjugate functions, we find after a little simplification that

$$p = \frac{\mu}{16c^2} [A\{-\frac{1}{4} \sinh 3\eta \cos 3\xi - \sinh 2\eta \cos 2\xi \\ - \frac{1}{4} \sinh \eta \cos \xi\} + B\{-\frac{1}{4} \cosh 3\eta \cos 3\xi \\ - \cosh 2\eta \cos 2\xi - \frac{1}{4} \cosh \eta \cos \xi\} - F\{2 \cosh 2\eta \cos 2\xi \\ + 8 \cosh \eta \cos \xi\} - 2L \sinh \eta \cos \xi] + \Pi_0.$$

It is clear that the pressure is finite everywhere.

*The Resistance.*

10. When  $\eta = \beta$ ,

$$\frac{\partial h^2}{\partial \xi} = -\frac{1}{8c^2} \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)^2} (2 \cosh \beta - \cos \xi) \sin \xi$$

$$\frac{\partial h^2}{\partial \eta} = \frac{1}{8c^2} \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)^2} (\cosh \beta - 2 \cos \xi) \sinh \beta$$

$$\frac{\partial^2 \psi}{\partial \xi^2} = -4cU \sinh \beta \left[ -\frac{\sin \xi}{(\cosh \beta + \cos \xi)^2} \right. \\ \left. + \frac{6 \sin \xi \cos \xi}{(\cosh \beta + \cos \xi)^3} + \frac{6 \sin^3 \xi}{(\cosh \beta + \cos \xi)^4} \right]$$

$$\frac{\partial^2 \psi}{\partial \xi \partial \eta} = -4cU \left[ \frac{\cosh \beta \cos \xi}{(\cosh \beta + \cos \xi)^2} + \frac{2 \cosh \beta \sin^2 \xi}{(\cosh \beta + \cos \xi)^3} \right. \\ \left. - \frac{2 \sinh^2 \beta \cos \xi}{(\cosh \beta + \cos \xi)^3} - \frac{6 \sinh^2 \beta \sin^2 \xi}{(\cosh \beta + \cos \xi)^4} \right]$$

$$\frac{\partial^2 \psi}{\partial \eta^2} = \sin \xi \left[ f_1(\beta) + \frac{f_2(\beta)}{(\cosh \beta + \cos \xi)^2} + \frac{f_3(\beta)}{(\cosh \beta + \cos \xi)^3} \right. \\ \left. + 24cU \frac{\sinh \beta \cosh \beta}{(\cosh \beta + \cos \xi)^3} - 24cU \frac{\sinh^3 \beta}{(\cosh \beta + \cos \xi)^4} \right]$$

while  $\frac{\partial \psi}{\partial \xi}$  and  $\frac{\partial \psi}{\partial \eta}$  are given by (C) and

$$f_1(\beta) = \left\{ \frac{9}{8}(A \cosh 3\beta + B \sinh 3\beta) + C \cosh \beta + D \sinh \beta \right\}$$

$$f_2(\beta) = \{-2(A \cosh 4\beta + B \sinh 4\beta) + 4F \sinh 2\beta\}$$

$$f_3(\beta) = \left\{ \frac{9}{8} \frac{5}{2}(A \cosh 5\beta + B \sinh 5\beta) - \frac{9}{8} \frac{5}{2}(A \cosh 3\beta \right.$$

$$+ B \sinh 3\beta) - \frac{9}{8} F \sinh 3\beta + J \sinh \beta$$

$$\left. + L(2 \cosh \beta + \beta \sinh \beta) \right\}.$$

Substituting in the expression for the rates of elongation of the shear, we find that

$$e = f = 0$$

$$\gamma = \frac{\sin \xi}{16c^2} \left\{ f_1(\beta) \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)} + f_2(\beta) \frac{(\cosh \beta + \cos \xi)^2}{(\cosh \beta - \cos \xi)} \right. \\ \left. + f_3(\beta) \frac{(\cosh \beta + \cos \xi)}{(\cosh \beta - \cos \xi)} \right\} + \frac{U}{4c} \sinh \beta \sin \xi \frac{(\cosh \beta + \cos \xi)}{(\cosh \beta - \cos \xi)}.$$

The resistance is given by

$$R = \int \left( p \frac{dy}{ds} - \mu \gamma \frac{dx}{ds} \right) ds$$

where the integration is taken round the boundary of the elliptic limacon.

Integrating, we have

$$R = 4\pi\mu U / (\beta - \tan h\beta)$$

My best thanks are due to Dr. N. M. Bose for the interest he has taken in the preparation of the paper.

*Note.*—Although it has been shown that the velocity is everywhere finite and continuous and the rate of change of velocity everywhere finite, yet it is found that the rates of changes of velocity, viz.,  $\frac{\partial \psi}{\partial x}$  and  $\frac{\partial \psi}{\partial y}$ , are discontinuous across the double lines  $\eta=0$ . Therefore the surface traction  $p_{xy}$  is discontinuous across  $\eta=0$ . It is probable that the motion is due to a prescribed velocity across the lines  $\eta=0$ . The phenomenon is a matter for subsequent examination. The detailed examination will follow later on.

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# CHEMISTRY



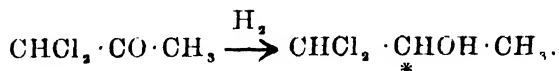
# The Reduction of Unsymmetrical Dichloracetone by Yeast

BY

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The reduction of chlorinated ketones does not appear to have been studied hitherto, although the reduction of aldehydes and ketones in general by yeast has been the subject of thorough investigation by Neuberg<sup>1</sup> and his co-workers. Their work conclusively proves the value of yeast as a reducing agent, which must play an important part in ordinary fermentation as also in natural syntheses. The first important example of biochemical reduction of this nature was furnished by Linter, Liebig, and Lüers who reduced chloral hydrate and made the preparation of trichlorethyl alcohol accessible in the laboratory. The importance of reducing monochloracetone, or indeed, of any of the unsymmetrical chloracetones by means of yeast, lies firstly in the fact that these acetones after reduction give rise to alcohols containing an asymmetric carbon atom as is evident from the following :



Secondly, these chlorinated secondary alcohols would form the basis of urethane derivatives, valuable as soporifics. In ordinary chemical reduction it is the

<sup>1</sup> C. Neuberg and J. Kerb. Ber. 46, 2225 (1913).

<sup>2</sup> C. J. Linter and H. J. V. Liebig H. 72, 449 (1911); Linter and Lüers. H. 88, 122 (1913).

racemic form that is invariably obtained, as the chance of formation of the dextro-form is equal to the chance of formation of the laevo-form. In the case of biochemical reduction, the chance of obtaining optically active components is usually great due to the selective action of enzymes, and if in any way the preponderance of one isomer over the other can be secured, the resulting compound should exhibit optical activity (compare Neuberg and Kerb; Neuberg and Nord). An early example of the selective action of ferments or bacteria is to be found in Le Bel's work on the fermentation of inactive propylene glycol by *bacterium termo*. A further example of interest is to be found in the work of Peré,<sup>1</sup> who studied the biochemical oxidation of propylene glycol in contact with *tyrothrix tenuis*. It is significant that this investigator obtained a dextro-rotating propyl glycol, as distinct from the laevo rotatory propyl glycol obtained by Le Bel. The explanation must evidently lie in the use of different bacteria, which would seem to indicate with a degree of certainty that the action of the two bacteria upon racemic propyl glycol is selective.

The particular reaction described in these pages is a case of reduction by yeast in a fermenting solution of sugar. Here also the yeast exerts a selective action and from unsymmetrical dichloracetone gives rise to an optically active dichlorisopropyl alcohol. The rate of this reduction, however, in the case of dichloracetone is relatively rapid as the reduction is probably completed in 24 hours if not in 12 hours. The operation of adding a 20 per cent. alcoholic solution of 10 grams dichloracetone to a fermenting solution of sugar requires 3-4 hours, after which the mixture is allowed to stand

<sup>1</sup> Annales de Institut Pasteur, 1896, II, 600-8.

overnight in an incubator at 35°C. Next morning the odour of dichloracetone is scarcely to be noticed in the reaction mixture, and the sugar is also found to have disappeared to the extent of 96-97 per cent. The further addition of yeast, or of yeast and sugar, is only to secure certainty of reduction of any dichloracetone that might have remained unacted upon. Dichloracetone does not seem to be appreciably poisonous to beer-yeast and the yield of dichlorisopropyl alcohol is not affected by the rate of addition of the dichloracetone to the fermenting sugar solution. In one experiment in which accidentally the stopper of the dropping funnel was dislodged, about half of the alcoholic solution of dichloracetone fell at once into the fermenting sugar solution without markedly affecting the rate of fermentation of the solution. This non-poisonous character of dichloracetone is convenient and also interesting in view of the fact that Willstätter has recently found bromal very poisonous to yeast and Neuberg (*loc. cit.*) found it necessary to add the aldehydes with which he experimented, very cautiously to the fermenting solution in order to get a good yield of reduction product. Also in some experiments with monochloracetone the rate of addition was found to be very important. The first experiment was conducted with monochloracetone supplied by Messrs. Kahlbaum of Berlin, an alcoholic solution of which had to be very cautiously added in order to maintain the fermentation of the sugar solution. In fact even with the utmost care, it was difficult to maintain a brisk fermentation throughout the addition, and towards the end the addition of monochloracetone had actually to be suspended, in view of the considerably decreased rate of fermentation. It is to be observed here that in course of further investigation, it was found that the monochloracetone supplied by Messrs.



Kahlbaum was not pure, but contained a considerably higher percentage of chlorine than is required by the formula. This may be due either to the presence of some dichloracetone, the boiling point of which closely approaches that of monochloracetone, or to small quantities of higher chlorinated products. The conclusion, therefore, is that either monochloracetone or the very small quantities of tri-, tetra-, or penta-, chlor derivative of acetone, are poisonous towards yeast, dichloracetone itself having scarcely any injurious effect. Experiments with monochloracetone alone could not be completed on account of the difficulty in obtaining a pure specimen of the substance. Its preparation has now been undertaken. In the case of monochloracetone something different occurs, as the peculiar penetrating odour of this compound remains for over a week, and indeed does not then entirely disappear. In our experiments we followed the conversion of monochloracetone into monochlorisopropyl alcohol by the disappearance of this unpleasant and tear-bringing odour. As already mentioned, the poisonous nature of monochloracetone or any component with which it is contaminated, is so marked that a little carelessness in the addition of its alcoholic solution to the fermenting sugar solution speedily stops the fermentation. It is significant that monochloracetone has a fatal action upon yeast, whereas dichloracetone has practically no such injurious action. A careful comparison of the various chloracetones with regard to their action on yeast would be of interest and it is hoped that a future communication may be made thereon.

Whilst in the cases cited above (Neuberg, Peré, Le Bel) the rotation in two experiments was not constant, with dichloracetone however, this has been found to be the same in five separate experiments that have up to now been performed.

An additional interest in obtaining unsymmetrical dichlorisopropyl alcohol by the biochemical method lies in the ease with which a good and cheap yield of this alcohol can be obtained, rendering the process thereby suitable for practical application.

Several experiments have up till now been performed both with the alcohol itself and its urethane derivative, upon rabbits, which justify the expectation that they will be valuable as soporifics. It is to be observed that dichlorisopropyl alcohol is likely to have an advantage over chloral, being poorer in chlorine, and more effective than trichlorethyl alcohol, being a secondary alcohol. All experiments, that as yet it has been possible to conduct, show that both the alcohol and the urethane derivative are without any injurious effect upon the animal system, and that the difference between the narcotic and toxic doses is fairly considerable. A more detailed report of the investigation in this direction will be shortly communicated.

#### EXPERIMENTAL.

250 grams of starch sugar or ordinary cane sugar were dissolved in 2.5 litres of tap water at 40° in a 5-litre bottle. To the solution 250 grams of pressed beer-yeast were added. In about fifteen minutes the liquid was in brisk fermentation, when a 25 per cent. alcoholic solution of 10 grams dichloracetone was drop by drop added to the fermenting mixture, care being taken not to suppress the vigorous fermentation by too quick addition of the dichloracetone solution. In three to four hours the addition is complete, during which time the bottle is shaken from time to time. The reaction vessel is then allowed to stand overnight in an incubator at 35° C. Next morning the odour of dichloracetone

is found to have practically disappeared, and the sugar also almost fully used up. In order to ensure more complete reduction, about 100 grams more yeast are added and left again in the incubator for two more days, at the end of which the liquid is filtered, the residue washed two or three times and the combined filtrate distilled under vacuum on a boiling water-bath. The ethyl alcohol, dichlorisopropyl alcohol and any unchanged dichloroacetone being volatile in steam, collect in the receiver which is constantly kept well-cooled by a rapid current of tap water. The distillate is now shaken up with two litres of ether, the ethereal layer separated, dried over ignited sodium sulphate, and distilled off from a water-bath. The residue which now amounts to 8 cc. is fractionated from a small distilling flask, when 5.2 grams of dichlorisopropyl alcohol collect steadily at  $146^{\circ}$ - $148^{\circ}$  [compare Wohl and Roth, Ber., 40, 217 (1907)]. The fore-fraction also contains about a gram of the dichlorisopropyl alcohol identified by its optical rotation. From a large scale experiment with 48 grams of dichloroacetone, 26 grams of the pure alcohol were obtained, which correspond to a yield of 54 per cent. of the theory.

Dichlorisopropyl alcohol is moderately soluble in water and very soluble in ether and alcohol. It has a burning sweet taste, and a pleasant ethereal odour, having a density of 1.33. The pure liquid in a one-decimeter tube rotates the plane of polarisation by  $-11.88^{\circ}$ .  $[\alpha]_D$  is therefore  $-9^{\circ}$ .

Found C=27.83, H=4.76, Cl=54.0;  $C_3H_5OCl_2$  requires

C=27.91, H=4.65, Cl=55.0 per cent.

The urethane derivative 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CHCl}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{NH}_2 \end{array}$$
 is

prepared by mixing an ethereal solution of carbamyl chloride with the calculated quantity of dichlorisopropyl alcohol also in ethereal solution. The solution is allowed to stand at room temperature for 15 minutes, after which the ether is expelled on the water-bath. The residual oil soon solidifies on scratching with a glass rod and can then be crystallised either from ether in which it is extremely soluble, or from water in which it is soluble only to the extent of 2 per cent. at ordinary temperature. This is a decided advantage as the loss in crystallising from ether is excessive. The urethane crystallises in white needles, melting at  $61^{\circ}$ - $63^{\circ}$  C.

0.1330 gave  $N = 9.4$  cc., at  $16^{\circ}$  C and 755 mm. press.;  $N = 8.20$ ;  $C_4H_7O_2NCl_2$  requires  $N = 8.14$  per cent. 0.75 gram of the urethane dissolved in 25 cc. of water and 2 cc. of glycerine when given to a rabbit weighing 4.5 pounds caused an uninterrupted sleep for 11 hours. The parent alcohol given in 0.5 gram caused an undisturbed sleep in the same animal for a period of one hour, without spasms. The urethane derivative is also optically active, rotating the plane of polarisation to the left. 0.3336 gram dissolved in 2 cc. of absolute alcohol, rotated the plane through  $-2.226^{\circ}$  in a 1 dm. tube. The reduction of monochloracetone (from Kahlbaum) by a method similar to that adopted in the case of dichloracetone, resulted in a yield of not more than 25° per cent. In fractionating the final product of reduction after extraction with ether the first part of the distillate, after expulsion of the ether distilled under  $100^{\circ}$  C and contained mostly ethyl alcohol; the fraction distilling between  $100^{\circ}$  and  $125^{\circ}$  contained unconverted monochloracetone and also a small quantity of monochlorisopropyl alcohol,  $CH_2Cl \cdot CH(OH) \cdot CH_3$  the boiling point of which latter is  $127^{\circ}$ . Then came a fraction boiling between  $126^{\circ}$  and  $132^{\circ}$  which may be taken as more or less pure monochlorisopropyl alcohol,

but the thermometer then rose rapidly, a product boiling between  $138^{\circ}$  and  $152^{\circ}$  was collected which probably marks the boiling point limits of a mixture of mono- and dichlorisopropyl alcohol. After this the thermometer rose steadily up to  $180^{\circ}$  and a few drops of liquid of unknown composition were obtained.

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# On An Experimental Test of Thermal Ionisation of Elements.

BY

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Though the theory of thermal ionisation of gases has been given by one of the authors in a number of papers<sup>1</sup> about three years ago, its application has hitherto been confined mostly to the realm of astrophysics. The theory still lacks experimental confirmation in the laboratory, and the present communication is the outcome of an attempt just to remove this desideratum.

The underlying idea may be thus stated :—

If we take any element in the vapour state, and go on heating it, its electrical and optical properties will undergo a gradual change. To visualize matters, let us start with Ca-vapour at 800°C. At such a low temperature, it is most probably a non-conductor of electricity and will show only the lines  $\lambda=4227$ , 1S—2P,  $\lambda=6573$ , 1S—2p<sub>2</sub>, and other lines of the principal series in absorption. If we go on heating the gas, a stage will come when an appreciable fraction will be ionised. The vapour space will now conduct electricity, and will show the principal lines of Ca<sup>+</sup>,  $\lambda=3968$ (H), and  $\lambda=3933$ (K) in absorption. Between these two stages, the lines of subordinate series of Ca may also come out in absorption.

For sometime past, one of the authors has been trying to follow this process in the laboratory. The first attempt

<sup>1</sup> Proc., Roy. Soc. Lond., Vol. 99, p. 136, *et. seq.* Zs. f. Physik, Vol. 6, p. 40.

was made with the vapours of the alkali metals, because as these elements possess the lowest ionisation-potentials, it was expected that they would be copiously ionised even at such low temperatures as  $800^{\circ}\text{C}$ — $1000^{\circ}\text{C}$ . But it may be mentioned here that these metals are not suitable for the spectroscopic test, as their chief ionised lines lie far down in the ultraviolet.

The experiments on the electrical conductivity of heated alkali vapours were first undertaken at the laboratory of Prof. Nernst at Berlin, and the preliminary results which we obtained quite confirmed our expectations. It was found that Cs-vapour<sup>1</sup> at  $1250^{\circ}\text{C}$  possessed an enormous specific conductivity of  $(50\text{ ohm})^{-1}$ , which diminished gradually as the temperature was lowered, and at  $850^{\circ}\text{C}$ , was certainly smaller than  $(10000\text{ ohm})^{-1}$ . It was also found that the specific electrical conductivities were in the order  $\text{Cs} > \text{R} > \text{K} > \text{Na}$ , just as their ionisation-potentials would lead us to expect.

The furnace in which these experiments were carried out was not suitable for combined electrical and optical investigation as described above. Moreover, according to theory, the fraction of atoms ionised is a function of not only the temperature, but also of pressure. Hence it is desirable that a furnace be designed in which both temperature and concentration can be varied at will. In Nernst's furnace, pressure could not be varied at all.

In order to remove these defects, another arrangement was devised, which is described below.

This consists of two furnaces in vacuum. The material which is experimented upon is placed within the

<sup>1</sup> Lewis reports in his *Thermodynamics* (p. 460) that Urey carried out at his suggestion a similar experiment on the electrical conductivity of heated Cs-vapour. The full details of the paper are not yet available. The experiment mentioned above is fully described in the Journ. Dept. of Science, 1922, Calcutta University.

small furnace, which is heated to a varying temperature. The vapour pressure of the substance is known from this temperature. The substance in the vapour form is led to the bigger furnace which is maintained at a higher temperature. The volume within the big furnace containing heated vapour forms the experimental space, of which the electrical and spectral properties are studied. The great advantage in this type of furnace is that they allow both the temperature and concentration to be varied at will, which is not possible in the type used by A. S. King in the Mount Wilson Solar Observatory.

### THE FURNACE.

The furnace is shown diagrammatically in fig. 1. It is simply an adaptation of Prof. Compton's furnace (described in the Journ. Opt. Soc. America, Oct., 1922), with some modification to suit our convenience.

B=A rectangular hollow brass base, made of thick sheets of brass cooled by water, by inlet and outlet pipes at P and P<sup>1</sup>.

T=Heavy box of cast iron in the form of a rectangular parallelepiped, open at the bottom, and provided with flanges on all sides at the bottom for air-tight contact with the brass base. The joint was kept airtight by a preparation of resin and bee's wax.

M, M<sup>1</sup>=Projecting tubular pieces, of one piece with the box, and closed by glass or quartz plates, which are cemented to it by means of shellac.

L=Removable circular lid with a ground conical periphery and fitting into a ground, and sloping circular opening on the top of T. By taking out L, easy readjustments could be quickly made in the interior. This was just to avoid taking off the whole box T after every experiment for the necessary readjustments. The two



surfaces of contact were ground with great care till they fitted exactly into each other.

F=Furnace which in the preliminary experiments consisted of a sheet of iron rolled into the form of a circular tube. It was clamped by means of a headpiece and screws on the water-cooled stands,—S and S' which consist of thick iron tubes with a rectangular top of solid iron. The stands were water-cooled as shown in the diagram. The surface of the sheets was cleaned by the pickling process used in enamelling and then smoothed by emery paper.

D=A thick wire of iron, clamped on the stand 's' at one end and sliding in a groove at the head of the stand s' at the other end.

About half the space inside the furnace F was clear.

A current of 500-1000 amperes was applied to F under 6-10 volts directly from a battery of accumulators with a sliding resistance of mercury. Owing to the large size of the furnace, and the limited energy supply at our disposal, the temperature could not be raised higher than  $1250^{\circ}\text{C}$ , as eye observations would indicate. A low tension transformer as used by King would have been much better, but as we had not the means to buy one, we had to make the best use of a set of discarded storage cells. One great disadvantage was that after about 5 minutes the connecting wires became very hot, and less current flowed through F, and temperature rapidly fell. This defect would probably be cured if the furnace could be heated by current from a low-tension transformer, with very short and water-cooled leads. The furnace was evacuated by a Gaede oil pump, which was kept continuously running during the experiment. The leak was so small, that even at a temperature of  $1250^{\circ}$ , iron did not appreciably oxidise though the experiment lasted from 5-10 minutes.

$f$  = Another furnace of much smaller dimensions, heated directly by current from accumulators, the substance which was to be vaporised was kept inside the furnace here. The ends were blocked by iron-plugs, through one of which passed a thermo couple of iron and constantan shielded by pyrex glass tubing.

$t$  = Small porcelain tubing, leading the vapour through an orifice at the top of  $f$  to the heated space inside  $F$ .

The connections to  $f$  for leading the heating current consisted of thick copper rods (not shown in the diagram) passing through an India rubber cork, which closed an orifice at  $B$ . The leads for thermo couple were also taken through this cork.

The temperature to which  $f$  was heated could be obtained from the readings on the millivoltmeter to which the couple was connected. Then from the data on the variation of vapour pressure with temperature, the pressure in  $f$  could be obtained. The pressure in  $F$  is equal to that in  $F$ , if the free flow could be prevented by stopping the ends of  $F$  by quartz plates. This has not yet been attempted.

By this arrangement, it was hoped that the vapour of any element could be maintained at a definite pressure for any length of time. Experimental difficulties have, however, not been completely overcome, but the progress hitherto made has been sufficient to justify the expectations placed in this arrangement.

#### DESCRIPTION OF THE ARRANGEMENT FOR MEASURING THE ELECTRICAL CONDUCTIVITY.

The arrangement for measuring the electrical conductivity is shown in diagram No. 2.

$B$ —Battery.

$V$ —Voltmeter for measuring the potential difference between the central wire and the furnace.

F—Furnace.

R—Resistance for varying the voltage.

$K_1$ ,  $K_2$ —Two three-way keys.

M. A—is a milliamperemeter placed between one set of knobs of  $K_1$  and  $K_2$ .

Mic. A—is a microamperemeter placed between another set of knobs.

G—is a sensitive galvanometer placed between another set of knobs, with a variable megohm in series. By manipulating the keys  $K_1$ ,  $K_2$ , the furnace may be connected either through the milliammeter, the microammeter or the galvanometer. Voltage divided by the current gives the resistance of the vapour-space in the furnace.

#### ACTUAL EXPERIMENT.

The results which are communicated here are only of a preliminary nature.

The actual procedure was as follows :

Firstly, the central furnace was heated, and the thermionic current between the furnace and the central wire was measured. In most cases, this could be done by means of the galvanometer.<sup>1</sup> The thermionic current is a very good indication of the temperature of the furnace F. Then current was applied to the small

<sup>1</sup> It will be interesting in this connection to recall the experiments of Pring and Parker who investigated the thermionic emission from large carbon rods by heating them with the aid of very large currents. They found that with larger currents thermionic emission died down. Richardson pointed out that this was due to the large magnetic field of the heating current, which prevented the electrons to escape from the heated surface. In our experiment, though we are using currents of the order of  $10^3$  Amp, the experiment is being performed *inside* the heated space, where the magnetic field is zero, so that there is free thermionic emission. Incidentally, it may be mentioned that in this method the temperature of the emitting surface can be more precisely measured, if we direct the optical pyrometer to the interior, for radiation coming from inside the furnace approximates to the black body condition. The point is receiving attention.

furnace *f*. The substance vaporised, and the vapour passed into F. Then the observer at the galvanometer noted whether the spot of light in the galvanometer scale shifted its position. Simultaneously, another observer noted the readings on the millivoltmeter connected with the thermocouple.

If the spot of light went off the scale, the galvanometer circuit was shunted off, and the microammeter circuit was put in, and the current observed. If this did not suffice, the milliammeter circuit was inserted.

The pump was kept running during the whole course of the experiment, which generally took from 5 to 10 minutes.

When experiment with one substance was finished, and the furnace cooled down the lid was taken off. Then the small furnace *f* was replaced by a fresh one, because the old furnace is generally contaminated by deposits of the metal with which the previous work has been done. The big furnace F was replaced, only if it was broken, as frequently happened, probably owing to stress developed during expansion.

### *Series 1. Experiments with Hg, Cd and Zn.*

These three metals are interesting, because the electrical conductivity of their vapours in a flame were investigated by McLennan<sup>1</sup> a few years ago. The electrical conductivity of heated mercury vapour has formed the subject of investigation by many workers including Maxwell, Hittorff, J. J. Thomson and Strutt, but the results were mutually contradictory. McLennan's results also were quite indecisive.

We have proved decisively that when vapours of these elements are introduced into the furnace, between

<sup>1</sup> Proc. Roy. Soc., Lond., Vol. 92, p. 592.

the temperature  $850^{\circ}\text{C}$  to  $1300^{\circ}\text{C}$ , the thermionic current remains completely unaltered. The voltage applied was 1.34, and at the highest temperature employed by us ( $1300^{\circ}$  as judged by visual observation), the thermionic emission was 10 microamperes, with  $R=9000$  ohm in series. The temperature of the small furnace was  $650^{\circ}\text{C}$ , corresponding to a vapour pressure of 27.23 mm. of Zn. It was found that when Zn-vapour was evolved, there was not only no increment in the thermionic current but there was actually a slight falling off, owing probably to the cooling of the furnace by the passing Zn vapour. The same phenomena was observed with Hg and Cd, the last being operated at a temperature of  $740^{\circ}\text{C}$ , vapour pressure = 557.2 mms. of mercury.<sup>1</sup>

These experiments prove conclusively that vapours of Zn, Cd, and Hg are not ionised at all by heat up to temperatures of  $1250^{\circ}\text{C}$ . This is quite expected as the ionisation-potential of these elements are rather high, viz., 9.45, 9.40, 10.45 volts.

#### *Experiments with Mg and Ca.*

*Magnesium.*—The small furnace was heated to  $750^{\circ}$  (measured), and the large furnace to about  $1300^{\circ}\text{C}$  (not measured). The thermionic current was  $10 \times 10^{-6}$  amperes. On putting Mg-vapour, the current rose to  $\frac{2}{10}$  of a milliampere, or  $200 \times 10^{-6}$  Amp. or by about 20 times, so that magnesium vapour seems to have been ionised at  $1300^{\circ}\text{C}$ .

*Calcium.*—The small furnace was maintained at  $920^{\circ}\text{C}$  (measured), but the storage cells having run down, the temperature in the big furnace F could not be increased. It was probably  $1150^{\circ}\text{C}$ . The thermionic emission was less than a microampere, but on putting

<sup>1</sup> These figures are taken from Landolt and Bornstein's tables, 6th edition, pp. 1332-1338.

**Ca-vapour**, it rose to 30 microamperes. This proves that **Ca-vapour** is appreciably ionised at 1100°C.

*Sodium.*

**Sodium.**—The small furnace was maintained at 470°C, corresponding to a vapour pressure of about 2 mm. of mercury. The temperature in the big furnace was about 900°C. The thermionic emission amounted to 40 divisions on the galvanometer scale corresponding to a total resistance  $5 \times 10^6$  ohms. As one megohm was put in the galvanometer circuit, the resistance of the furnace-cell was approximately  $4 \times 10^6$  ohms. On putting **Na-vapour** the spot went off the scale at once, so that the micro-ampere circuit was put in. Even this went off the scale. Then the milliamperemeter circuit was put in with no resistance in series. The current was  $\frac{1}{10}$  of a milliamperere, so that the equivalent resistance with **Nx-vapour** was only 13400 ohms. Thus at 900°C the conductivity of the space increases about three hundred times, when **Na-vapour** is put in.

The only objection which can be raised against the view that **Na** or **Ca-vapour** is ionised by heat is that the electrons emitted from the surface of the furnace F in falling to the central wire, produce fresh ions by collision. This possibility is excluded by the fact that the potential difference between the furnace and the central wire is only 1.34 volt, much lower than the ionisation potential of the elements investigated. But it may be contended that since the total potential fall between two ends of the furnace is from 6 to 10 volts, electrons emitted from the negative end may just slip along the surface and come out at the end with an energy corresponding to a voltage drop of 6 to 10.

Though we can think of such an eventuality the probability of its affecting the main results seem to be

rather remote. At least, in future experiments, efforts will be made to free the arrangement from the possibility of such an objection.

In conclusion, we wish to record our thanks to our colleague Mr. S. Bhargava, Reader in this University, for useful help in designing the apparatus and to Mr. K. Majumdar, Research Scholar, for help in taking observations.

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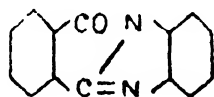
# The Colour of Complex Diazoles.

## Part I.

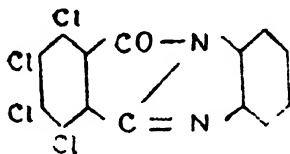
BY

GOPÂL CHANDRA CHAKRAVARTI.

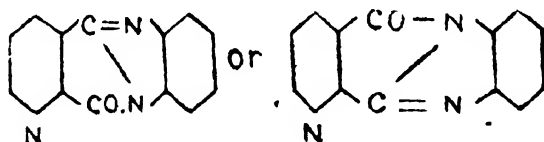
1 : 2-Orthobenzoylene-1 : 3-benzdiazole is obtained in a good yield by the fusion together of phthalic anhydride and o-phenylene diamine (Bistrzycki and Lecco, *Helv. Chim. Acta.*, 1921, 4, 425; compare also Thiele and Falk, *Annalen*, 1906, 347, 112; and Rupe and Thiess, *Ber.*, 1909, 42, 4287). Bistrzycki and Lecco (*loc. cit.*) applied the same method to the condensation of o-phenylene diamine with tetrachlorophthalic acid, and with quinolinic acid. 1 : 2-o-Benzoylene-1 : 3-benzdiazole



has been recognised to be a powerful chromophore and contains a fused pyrrol-iminazole ring in its skeleton. Both the diazoles, tetrachloro-1 : 2-o-benzoylene-1 : 3-benzdiazole,

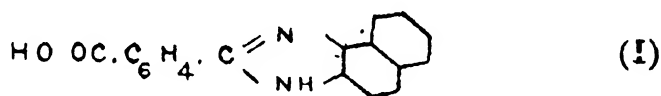


and 1 : 2-( $\alpha.\beta$ )-picolinoylene-1 : 3-benzdiazole,





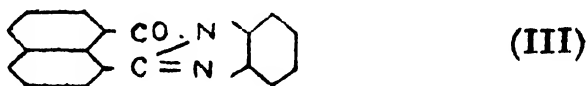
contain the fused pyrrol-iminazole ring systems but whereas the former is coloured greenish-yellow the latter is absolutely colourless. This absence of colour in the picolinoylene compound may be due to the strong hypsochromic character of the pyridyl nitrogen atom (compare Ghosh, T., 1919, 115, 1103) which neutralises the chromophoric nature of the pyrrol-iminazole system. These important chromogenic properties of the fused heterocyclic system led the present author to investigate the properties of a series of analogous compounds which contained the pyridine-iminazole skeleton. With this view, as also with the object of studying the influence of additional fused ring systems on the depth of colour of these compounds, intermediates already containing fused rings such as 1:8-naphthalic anhydride and 1:2-naphthylene diamine have been employed in the condensation. Phthalic anhydride combines with 1:2-naphthylene diamine in alcoholic solution (compare Hans Lieb, Monatsh, 1918, 39, 873), to form 1':2'-naphthiminazole-2-phenyl-o-carboxylic acid,



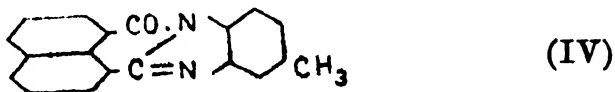
which on treatment with acetic anhydride or on being heated to a high temperature loses a molecule of water and is converted into 1:2-o-benzoylene-1:3-naphthadiazole,



The latter crystallises in beautiful orange-yellow prisms. 1:2-(1':8')-Naphthoylene-1:3-benzdiazole,



derived from naphthalic anhydride and *o*-phenylene diamine has an intense yellow colour. 1:2-(1':8')-Naphthoylene-1:3-(-2'')-methylbenzdiaazole

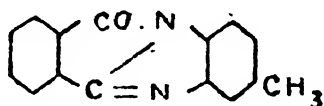


obtained from naphthalic anhydride and orthotoluylene diamine is coloured deeply yellow. The colour of 1:2-(1':8')-naphthoylene-1:3-(1'':2'')-naphthiminazole



obtained by the condensation of naphthalic anhydride with 1:2-naphthylene diamine is orange-red. All the compounds with formulæ III, IV and V contain a pyridine ring fused with an iminazole, one and all of them are intensely coloured. Thus like condensed pyrrol-iminazole ring systems, the pyridine-iminazoles also possess marked chromophoric properties. This is also borne out by the experiments of Bistrzycki and Fässler (Helv. Chim. Acta., 1923, 6, 519) who find that the compound obtained by the condensation of homophthalic anhydride with *o*-phenylene diamine is coloured.

1:2-Orthobenzoylene-1:3-(2')-methyl-benzdiaazole



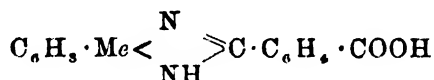
obtained by the condensation of phthalic anhydride with 1:3:4-*o*-toluylene diamine is found to resemble 1:2-*o*-benzoylene-1:3-benzdiaazole in colour. It thus appears that the effect of the presence of increasing fused ring systems is to deepen colour and that the naphthiminazoles

are generally more strongly coloured than the benziminozoles. A comparison of colour of these compounds will make the point clear.

1 : 2-orthobenzoylene-1 : 3-benzdiazole	...	Yellow.
1 : 2-orthobenzoylene-1 : 3-methylbenzdiazole	...	Do.
1 : 2-o-benzoylene-1 : 3-naphthadiazole	...	Orange-yellow.
$\alpha\beta$ -diphenylacrylenebenziminazole	...	Brown.
(Bistrzycki and Fässler, <i>loc. cit.</i> )		
O-phenyleneacetyl-2 : 1-benzimidazole	...	Yellow.
(Bistrzycki and Fässler, <i>loc. cit.</i> )		
Tetrachloro-1 : 2-o-benzoylene-1 : 3-benzdiazole	...	Greenish-yellow.
(Bistrzycki and Lecco)		
1 : 2-(1' : 8')-naphthoylene-1 : 3-benzdiazole	...	Deep yellow.
1 : 2-(1' : 8')-naphthoylene-1 : 3-methyl-benzdiazole	... ..	Do.
1 : 2-(1' : 8')-naphthoylene-1 : 3-naphthiminazole		Orange-red.

### EXPERIMENTAL.

*Condensation of Phthalic Anhydride with 1 : 3 : 4-o-Toluylene Diamine. The Formation of Toluyleneamidine-benzenyl-o-carboxylic acid.*—



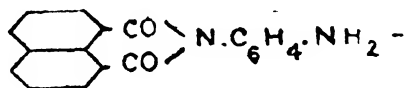
Identical with the compound obtained by Bistrzycki (B. 23, 1042-1046) by the treatment of o-toluylene diamine with phthalaldehydic acid, is prepared by mixing together 3 gms. of the anhydride, 2.6 gms. of the diamine and 40 c.c. of absolute alcohol. The mixture is refluxed on the water bath for nearly 3 hours and allowed to cool. The residue is filtered off, washed with a little alcohol and ether and crystallised from 50% acetic acid. It has the melting point 260-262°. It is insoluble in water, chloroform, acetone, ether and toluene. It dissolves fairly in

mineral acids and also in alkalis and alkaline carbonates. (Found: C=71.18; H=4.51.  $C_{15}H_{12}N_2O_2$  requires C=71.43; H=4.76 per cent.).

*1:2-Orthobenzoylene-1:3-methylbenzdiazone (VI).—*The amidine carboxylic acid described above is heated in a dry tube when the diazole partly sublimes and condenses on the cooler part of the tube. This is scraped off and crystallised from absolute alcohol. The crystals are yellow and melt at 166°. They dissolve in concentrated sulphuric acid giving a yellow solution with a green tint. (Found: C=76.75; H=4.50.  $C_{15}H_{10}N_2O$  requires C=76.92; H=4.27 per cent.).

*1':2'-Naphthiminazole-2-phenylorthocarboxylic Acid (I).—*Lieb (*loc. cit.*) obtained this compound as a by-product during the preparation of diphtalyl-1:2-naphthylene diamine. But by boiling an absolute alcoholic solution of phthalic anhydride and 1:2-naphthylene diamine in equimolecular quantities for three to four hours, nearly a quantitative yield of the acid is obtained. The product of the reaction is cooled, the precipitate filtered off and repeatedly extracted with hot alcohol and acetone. The residue is then finally crystallised from nitrobenzene. The crystals melt above 300°. (Found: C=75.21; H=4.30.  $C_{18}H_{12}N_2O_2$  requires C=75.00; H=4.16 per cent.).

*Condensation of Naphthalic Anhydride with Orthophenylene diamine—the Formation of Orthoaminonaphthalanil:—*



Three grams of the diamine are dissolved in 60 c.c. of absolute alcohol and five grams of naphthalic anhydride are then added to it. The mixture is then boiled under

reflux for 6—8 hours. On cooling the precipitate is filtered off and crystallised from acetone. The product is treated with sodium carbonate solution. The undissolved residue washed with hot water, melts at about  $245^{\circ}$  with decomposition with previous softening. (Found :  $C=74.92$  ;  $H=4.25$  ;  $N=9.57$ .  $C_{18}H_{12}N_2O_2$  requires  $C=75.00$  ;  $H=4.16$  ; and  $N=9.72$  per cent.). The alkaline extract on acidification with concentrated hydrochloric acid yields silky needles of benziminazole-2-naphthyl-8'-carboxylic acid melting at  $265-269^{\circ}$ .\* (Found :  $N=9.61$ .  $C_{18}H_{12}N_2O_2$  requires  $N=9.72$  per cent.).

*Acetyl Derivative.*—The orthoaminonaphthalanil is dissolved in pyridine, acetyl chloride is added to it drop by drop and the mixture allowed to stand for about half an hour. On pouring the liquid into water and stirring with a glass rod the acetyl derivative solidifies. It is then crystallised from glacial acetic acid. It has the melting point  $224^{\circ}$ . (Found :  $C=72.50$  ;  $H=4.63$ .  $C_{20}H_{14}N_2O_2$  requires  $C=72.72$  ;  $H=4.24$  per cent.).

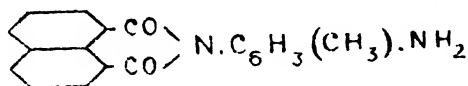
*Benzoyl Derivative.*—The orthoaminonaphthalanil is dissolved in pyridine and drop by drop an excess of benzoyl chloride added to the solution. It is allowed to stand for 10 minutes and a small quantity of hot water is added to it. The benzoyl derivative which crystallises out in yellow needles is recrystallised from pyridine and water. It melts at  $209^{\circ}$ . (Found :  $C=72.86$  ;  $H=4.52$  ;  $C_{25}H_{18}N_2O_4$  requires  $C=73.17$  ;  $H=4.40$  per cent.).

*N-Ethyl Derivative.*—The orthoaminonaphthalanil is heated under reflux with excess of ethyl iodide for 6—8 hours. Then the excess of ethyl iodide is evaporated off and the product crystallised from alcohol. It melts at  $235-37^{\circ}$ . (Found :  $C=75.69$  ;  $H=5.36$ .  $C_{20}H_{16}N_2O_2$  requires  $C=75.95$  ;  $H=5.06$  per cent.).

\* All these compounds on heating are transformed into the corresponding diazoles. H<sub>2</sub> melting points often are found to be not very sharp.

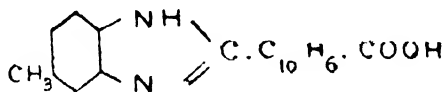
*1 : 2-(1' : 8')-Naphthoylene-1 : 3-benzdiazole (III).—*The orthoaminonaphthalanil or the benziminazole-2-naphthyl-8'-carboxylic acid is heated at a temperature of 210—220° in an oil bath for about 2—3 hours. The substance gradually softens and finally becomes liquid. It is allowed to cool and extracted with absolute alcohol from which medium the diazole crystallises in deep yellow needles m. p. 198°. (Found: C=79.93; H=3.88.  $C_{13}H_{10}N_2O$  requires C=80.00; H=3.70 per cent.). The same change occurs if either the anilide or the acid be boiled with acetic anhydride.

*Condensation of Naphthalic Anhydride with Orthotoluylene Diamine.*—4 gms. of naphthalic anhydride are mixed with 2.6 gms. of orthotoluylene diamine and 50 c.c. of absolute alcohol. The mixture is boiled on the water-bath for 6 hours. After allowing to cool the precipitate is filtered off and washed with a little alcohol. It is then extracted with boiling xylene. The xylene solution shows intense green fluorescence and on cooling deposits bright yellow crystals of orthoaminotolynaphthalimide,



m. p. 196°. (Found: C=75.31; H=4.52.  $C_{19}H_{14}N_2O_2$  requires C=75.50; H=4.63 per cent.).

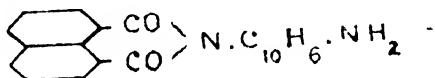
*Toliminazole-2(1')-naphthyl-8'-carboxylic Acid,*



The residue after extraction with xylene in the above experiment is dissolved in alkali, filtered and the solution neutralised with hydrochloric acid. The colourless crystalline product is filtered off, washed with water and dried. It melts at 273—75°. (Found: C=75.58; H=4.81.  $C_{19}H_{14}N_2O_2$  requires C=75.50; H=4.63 per cent.).

*1 : 2-(1' : 8')-Naphthoylene-1 : 3-methylbenzdiazole (IV).*  
 —When the o-aminotolynaphthalimide is heated in a tube a deep yellow product boils over and condenses in the cooler part of the tube. The latter is crystallised from alcohol into deep yellow needles m. p. 187°. (Found : C=80·11 ; H=4·60.  $C_{19}H_{12}N_2O$  requires C=80·28 ; H=4·22 per cent.).

*Condensation of Naphthalic Anhydride and 1 : 2-Naphthylene Diamine—the Formation of 2'-Amino-N-(1')-naphthyl-naphthalimide.*—



Equimolecular quantities of the anhydride and the diamine are mixed with absolute alcohol and boiled for 10—12 hours. The brown precipitate is filtered off and extracted with alcohol, acetone and carbon bisulphide. The residue is finally crystallised from nitrobenzene. M. p. above 300°. (Found : C=77·79 ; H=3·98.  $C_{22}H_{14}N_2O_2$  requires C=78·10 ; H=4·14 per cent.).

*1 : 2-(1' : 8')-Naphthoylene-1 : 3-naphthiminazole (V).*—The naphthalimide described above distills over on heating. The solid product is extracted with absolute alcohol which on cooling deposits beautiful orange-red crystals m. p. 256°. It dissolves in concentrated sulphuric acid giving an yellow solution with intense green tint. (Found : C=82·24 ; H=4·51.  $C_{22}H_{12}N_2O$  requires C=82·50 ; H=4·37 per cent.).

Further investigation to establish a relation between the colour and constitution of the diazoles is being carried on.

In conclusion, the author's best thanks are due to Sir P. C. Ray for his kind interest and encouragement during the progress of the investigation.

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# Thiodiazines.

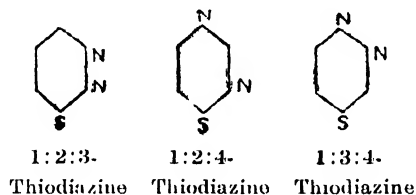
## Part I.

### Condensation of Thiosemicarbazide with *o*-Bromacetophenone.

BY

PRAFULLA KUMAR BOSE.

Thiodiazole derivatives have been studied by numerous investigators chiefly by Max Busch and his collaborators, but there is lack of information regarding the chemistry of thiodiazines. An examination of the literature showed that of the six possible classes of thiodiazines, a few representatives of the following three types only are known, nam



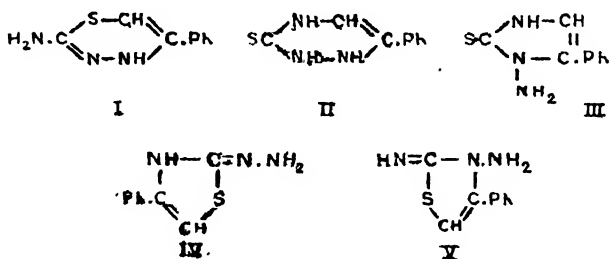
Schrader (J. pr. Chem., 1917, [2], 96, 180) obtained a derivative of 1:2:3-thiodiazine by condensing *o*-cyano-benzenesulphonyl chloride with hydrazine. Again a derivative of 1:2:4-thiodiazine has been obtained by the oxidation of 2-phenylimino-3-phenyl-tetrahydrothiazole, (Kucera, Monats., 1914, 35, 137; compare also Schrader, J. pr. Chem., 1916, [2], 95, 392); while the only derivative of 1:3:4-thiodiazine is that obtained by Frerichs and Förster (Annalen, 1910, 371, 236, 255). It might be mentioned here that the so-called 1:3:4-thiodiazines obtained by the condensation of potassium aryl-sulphocarbazines with ethylene dibromide (Busch, Ber., 1894, 27, 2509, 2516; Busch and Lingenbrink, J. pr. Chem., 1899, [2], 60,



219, 225) have afterwards been proved to be arylhydrazones of cyclic dithiocarbonic ester (Busch and Lingenbrink, J. pr. Chem., 1902, [2], 65, 473). Another so-called thiodiazine derivative, 2-amino-4-phenyl-5-ketodihydro-1 : 3 : 4-thiodiazine obtained by condensing phenylhydrazine with sulphocyanacetic acid (Harries and Klamt, Ber., 1900, 33, 1154) has been shown by Frerichs and Förster (*loc. cit.*) to be a thiohydantoin derivative. Evidently, excepting the very few derivatives of the thiodiazines referred to above, no other representatives of this class of compounds are known. An investigation has therefore been taken up with a view to obtain further knowledge on the subject. In the present communication, which is of a preliminary character, the condensation of thiosemicarbazide with  $\omega$ -bromacetophenone has been described and the constitutions of the reaction products determined.

On boiling an alcoholic solution of the reactants in molecular proportion, the hydrobromide of a base of the empirical composition,  $C_9H_9N_3S$  (m. p.  $125^\circ$ ) separates in brownish-yellow needles melting at  $196^\circ$ , while the mother liquor on being treated with acetone in the cold gave a crystalline hydrobromide (m. p.  $225-26^\circ$  not sharp,) of another compound of the empirical formula  $C_{11}H_{13}N_3S$  which melted at  $123^\circ$ .

The condensation of  $\omega$ -bromacetophenone with thiosemicarbazide might lead to the formation of the following possible isomeric compounds.



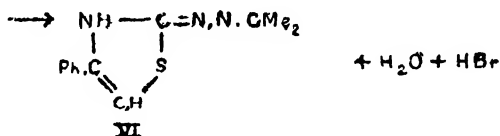
The absence of acid character of the substance, (m. p.  $125^{\circ}$ ), coupled with its inability to lose sulphur when boiled with alkaline lead solution or freshly precipitated yellow mercuric oxide, precludes the possibility of its possessing a  $\text{-NH-CS-NH}$  or  $\text{-NH-CS-N=}$  residue in the molecule as represented in formulæ (II) and (III) (compare Guha, J. Am. Chem. Soc., 1922, 44, 1511). Moreover, it is well-known that a halogenated ketone acts on thiocarbamides forming compounds containing sulphur atom in the ring (compare Walther and Roch, J. pr. Chem., 1913, [2], 87, 27). Again the compound under discussion has been found lacking in the capacity to condense with acetone or anisaldehyde, which should not be the case, had it possessed any free hydrazino group as formulated in (IV) and (V). On the other hand, the chemical evidence based on its actions towards phenylthiocarbimide, carbon disulphide and benzene sulphonyl chloride points definitely to the presence of a free amino group in the molecule. All these facts are best interpreted by the formula (I), which has consequently been assigned to the compound.

2-Amino-5-phenyl-1:3:4-thiodiazine (I) is a strong monoacid base and forms well-defined salts with acids. It gave a picrate and an aurichloride. The acetyl and benzoyl derivatives are soluble in alkali.

Attempt was made to prepare the isomeric acetyl compound, 2-amino-5-phenyl-3-acetyl-1:3:4-thiodiazine, by the action of  $\omega$ -bromacetophenone upon 1-acetylthiosemicarbazide. The reaction took place readily in alcoholic solution producing the hydrobromide of an acetyl compound which is soluble in alkali. The alkaline solution, however, unlike that of its isomer, develops a beautiful greenish-blue colour on exposure to air, which turns pink on being acidified. On boiling with an excess of dilute hydrochloric acid, the acetyl compound

suffered a smooth hydrolysis yielding a crystalline base (m. p. 167-68°) isomeric with 2-amino-5-phenyl-1:3:4-thiodiazine (I). On further examination it was found to behave like substituted hydrazine since it readily condensed with acetone and anisaldehyde. The acetone condensation product appeared to be identical with the base,  $C_{12}H_{13}N_3S$  (m. p. 123°) obtained by adding acetone to the condensation product of thiosemicarbazide and  $\omega$ -bromacetophenone (*vide supra*). It might, therefore, be reasonably assumed that the reactions in both the cases have proceeded in such a way that the hydrazino residue of the thiosemicarbazide has been left unattacked. Consequently the constitution of the base, m. p. 167-68°, might be represented by (IV) or (V).

In order to obtain clear evidence in support of one or other of these two formulæ, acetone-thiosemicarbazone was condensed with  $\omega$ -bromacetophenone. The resulting hydrobromide, as also the base proved to be identical with the acetone condensation products mentioned before. Now acetone-thiosemicarbazone has been shown to react with alkyl halides producing compounds of the type  $NH_2 \cdot C(SAlk):N.N: CMe_2$  (Wilson and Burns, T., 1922, 121, 870). In other words, the hydrogen atom attached to the nitrogen atom in position 2, is responsible for the tautomeric thiol-form. From the close analogy therefore, one might expect that the condensation of  $\omega$ -bromacetophenone and acetone-thiosemicarbazone proceeds thus :



The base,  $C_{12}H_{13}N_3S$ , m. p. 123° is thus proved to be 2-keto-4-phenyl-2 : 3-dihydro-1 : 3-thiazole-isopropylene



derivative. The production of the acetyl derivative of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone from 1-acetyl-thiosemicarbazide and  $\omega$ -bromacetophenone confirms this deduction.

### EXPERIMENTAL.

*Thiosemicarbazide and  $\omega$ -Bromacetophenone: Formation of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene hydrazone (VI) and 2-Amino-5-phenyl-1:3:4-thiodiazine (I).*—4.5 grams (1 mol.) of thiosemicarbazide and 10 grams (1 mol.) of  $\omega$ -bromacetophenone were heated under reflux with 50 c. c. of dry ethyl alcohol for 15-20 minutes. The dark reddish-brown solution was then concentrated to nearly one-third its volume and cooled, when clusters of brownish yellow needles of the hydrobromide of (I) began to appear. These were freed from the mother liquor, washed with dry ethyl alcohol and finally with acetone. The yield of the crude hydrobromide, m. p. 192-95°, was about 8.6 grams or about 64% of the theoretical. The mother liquor was diluted with its own volume of dry acetone and the colorless plates (m. p. 225-26°) of the hydrobromide of (VI) which immediately began to appear, were collected after an hour. The yield was about 2.1 grams or about 14% of the theoretical. The latter hydrobromide was dissolved in hot water containing a few drops of methyl alcohol, filtered and the solution made alkaline with sodium carbonate. The crystalline precipitate of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene hydrazone (VI) was crystallised from dilute methyl alcohol in colorless hexagonal plates melting at 123°, which turned reddish brown on exposure to light for some time. (Found: C=62.20; H=5.85.  $C_{12}H_{13}N_3S$  requires C=62.35; H=5.63 per cent.).

The former hydrobromide (m. p. 192-95°) separates from a 95% alcoholic solution by the addition of ether, in snow-white needles melting at 197°, after the usual treatment with animal charcoal. (Found: N=15.27; Br=29.86; S=11.34.  $C_9H_{10}N_3SBr$  requires N=15.54; Br=29.41; S=11.77 per cent.). To obtain the free thiodiazine the crude hydrobromide (8.6 grams) was dissolved in about 150 c.c. of warm water and allowed to stand for an hour. The solution was then filtered to remove a small amount of a brownish yellow impurity and made alkaline with a solution of sodium carbonate. The solution at once turned milky and within a few minutes gave a mass of colorless needles of *2-amino-5-phenyl-1:3:4-thiodiazine* (I). These were filtered after half an hour, washed with cold water and dried on a porous plate. The compound was purified by repeatedly dissolving in cold dilute hydrochloric acid filtering off any insoluble matter and precipitating with dilute sodium carbonate solution. It melted at 125-26°. (Found: C=56.80; H=4.69; N=22.05; S=17.07.  $C_9H_9N_3S$  requires C=56.55; H=4.71; N=21.99; S=16.76 per cent.). The base is very soluble in most organic media from which it is difficult to obtain it in the crystalline form on dilution with suitable solvents. On exposure to air, (especially when moist) or in solution, it gradually turns brown owing to oxidation.

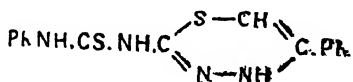
The *hydrochloride* of the base separates from a mixture of alcohol and ether in colorless rectangular plates melting at 205° decomp. (Found: Cl=15.44; S=14.18.  $C_9H_{10}N_3SCl$  requires Cl=15.60; S=14.07 per cent.). The *picrate* was obtained in the form of golden yellow plates melting at 215° decomp., on mixing the components in alcoholic or acetone solution. The *aurichloride* was obtained by treating a hydrochloric acid solution of the base with a dilute aqueous solution of auric

chloride. It crystallised from hot water in golden yellow needles melting at  $166-67^{\circ}$  decomp. (Found :  $\text{Au}=37.19$  ;  $\text{Cl}=26.30$ .  $\text{C}_9\text{H}_{10}\text{N}_3\text{SCL}_4\text{Au}$  requires  $\text{Au}=36.98$  ;  $\text{Cl}=26.79$  per cent.).

The *acetyl* derivative was obtained by treating the base with acetyl chloride in pyridine solution in the cold. From glacial acetic acid it separates in colorless needles melting at  $172-73^{\circ}$ . (Found :  $\text{N}=18.07$ .  $\text{C}_{11}\text{H}_{11}\text{ON}_3\text{S}$  requires  $\text{N}=18.03$  per cent.). The *benzoyl* derivative, obtained in a similar manner, crystallises from dilute pyridine in colorless needles melting at  $170^{\circ}$ . (Found :  $\text{N}=14.7$  ;  $\text{C}_{16}\text{H}_{16}\text{ON}_3\text{S}$  requires  $\text{N}=14.24$  per cent.). The acetyl and benzoyl compounds are soluble in aqueous alkali; acids precipitate them from solution in white amorphous mass.

*2-Amino-5-phenyl-1:3:4-thiodiazine and Methyl Iodide*.—A methyl alcoholic solution of the base was heated with an excess of methyl iodide under reflux for 5-6 hours on the water bath when the hydroiodide of 2-methylamino-5-phenyl-1:3:4-thiodiazine (?) separates in colorless needles. It was recrystallised from 95% alcohol and ether in colorless prismatic needles melting at  $223^{\circ}$  decomp. (Found :  $\text{N}=13.09$  ;  $\text{I}=39.11$ .  $\text{C}_{10}\text{H}_{12}\text{N}_3\text{SI}$  requires  $\text{N}=12.62$  ;  $\text{I}=38.14$  per cent.). The hydroiodide of the ethylation product, which crystallises in colorless rectangular plates and melts at  $234^{\circ}$  decomp., could be similarly obtained. These hydroiodides are soluble in hot water. On treating the aqueous solution with alkali or sodium carbonate colorless oils were obtained which failed to crystallise.

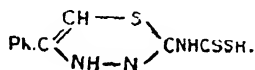
*2-Amino-5-phenyl-1:3:4-thiodiazine and Phenylthiocarbimide : Formation of*



The reactants were heated in alcoholic solution in molecular proportion for a few minutes, when yellow crystals of the above thiocarbamide separated out. From pyridine it was obtained in bright yellow plates melting at  $179-80^{\circ}$ . (Found:  $N=16.65$ .  $C_{16}H_{14}N_4S_2$  requires  $N=17.18$  per cent.).

*2-Phenylsulphonylamino-5-phenyl-1:3:4-thiodiazine.*—To one molecule of the above base were added two molecules of alcoholic caustic potash and then with constant shaking an alcoholic solution of one molecule benzene sulphonyl chloride. The reaction was completed by heating on the water bath for a few minutes. On cooling colorless needles were obtained. These were recrystallised from alcohol, the first fraction being rejected. The product which appeared to be the potassium salt of the complex sulphonamide was however not very pure. (Found:  $S=9.82$ .  $C_{15}H_{13}O_2N_3SK$  requires  $S=8.68$  per cent.). It was very soluble in water. The free sulphonamide could not be obtained pure owing to its hygroscopic nature and extreme solubility in water and other organic media.

*2-Amino-5-phenyl-1:3:4-thiodiazine and Carbon Disulphide: Formation of*



A mixture of the base (1 mol.), alcoholic caustic potash (1 mol.) and carbon disulphide in excess was heated on the water bath under reflux for 8-10 hours. The excess of carbon disulphide was distilled off, the liquid separated from a small amount of an oily residue and the free dithiocarbamic acid precipitated by acidifying with dilute hydrochloric acid. The yellow product was dissolved in aqueous alkali, treated with animal charcoal and reprecipitated by hydrochloric acid. From absolute



alcohol it separates in yellow needles melting at  $181-82^{\circ}$  decomp. (Found :  $N=15.97$  ;  $S=35.30$ .  $C_{10}H_9N_3S_3$  requires  $N=15.73$  ;  $S=35.96$  per cent.).

The *monomethyl* derivative was obtained by dissolving the dithiocarbamic acid in the calculated amount of methyl alcoholic potash and heating under reflux for half an hour with an excess of methyl iodide. The reaction mixture on being concentrated by evaporation deposited the methyl ether in bright yellow hexagonal plates, which melted at  $159^{\circ}$ , after crystallisation from dilute pyridine. (Found :  $C=46.76$  ;  $H=4.09$ .  $C_{11}H_{11}N_3S_3$  requires  $C=46.98$  ;  $H=3.92$  per cent.)

*1-Acetylthiosemicarbazide and  $\omega$ -Bromacetophenone : Formation of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetylhydrazone.*—Equimolecular quantities of the components were heated in *dry* alcoholic solution for a few minutes. On cooling the *hydrobromide of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetyl hydrazone* was deposited in colorless needles melting at  $234-35^{\circ}$  decomp. The hydrobromide was dissolved in 80 per cent. alcohol and treated with an excess of aqueous ammonia when the free acetyl compound was obtained. It separated from hot alcohol, after treatment with animal charcoal, in pinkish needles melting at  $196-97^{\circ}$  decomp. (Found :  $C=56.08$  ;  $H=5.16$ .  $C_{11}H_{11}ON_3S$  requires  $C=56.65$  ;  $H=4.72$  per cent.). The acetyl compound is soluble in alkali. The alkaline solution develops a beautiful greenish blue colour in presence of air, which turns pink when acidified. The colour totally vanishes after a few hours.

*Hydrolysis of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetylhydrazone.*—The acetyl compound was heated with a large excess of dilute hydrochloric acid (2N approx.) for about an hour until a test portion on being made alkaline with caustic soda and shaken with air did not turn blue. The whole solution was then made alkaline

with caustic soda when *2-keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone* (IV) was precipitated in dirty white needles. This was rapidly filtered at the pump, redissolved in dilute hydrochloric acid, filtered from a small amount of brown oxidation product and precipitated with sodium carbonate solution. It was finally crystallised from alcohol in long colorless needles melting at 167-68°. (Found: C = 56.00; H = 4.24.  $C_9H_9N_3S$  requires C = 56.55; H = 4.71 per cent.). It possesses strong basic properties and forms well-defined salts with acids. The moist base on exposure to air turns brown owing to oxidation.

*2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone and Acetone: Formation of* (VI).—The reactants were boiled together for a few minutes and the solution evaporated to dryness. The brown residue was taken up with methyl alcohol, decolorised with animal charcoal, and precipitated by cautious addition of water in hexagonal plates melting at 123°. The substance turns brown on exposure to light. (Found: N = 17.87.  $C_{12}H_{13}N_3S$  requires N = 18.18 per cent.).

*2-Keto-4-phenyl-dihydro-1:3-thiazole-anisal hydrazone.*—This was obtained by the condensation of *2-keto-4-phenyl-2:3-dihydro-1:3-thiazole hydrazone* and *anisaldehyde* as a beautiful yellow compound when a dilute hydrochloric acid solution of the hydrazone was shaken with *anisaldehyde*. From alcohol it separates in pinkish white needles melting at 225° decomp. (Found: N = 13.35.  $C_{17}H_{15}N_3S$  requires N = 13.59 per cent.).

*Condensation of Acetonethiosemicarbazone and  $\omega$ -Bromacetophenone: Formation of* (VI).—1.3 grams of the former and 2 grams of the latter were boiled under reflux with 30 c.c. of *dry* alcohol for about 15 minutes. The condensation product separated from the boiling mixture in colorless plates melting at 235° decomp., and appeared to be identical with the hydrobromide (m. p. 225-26° not

sharp) obtained by the addition of acetone to the mother liquor of the condensation product of thiosemicarbazide and  $\omega$ -bromacetophenone. The hydrobromide was dissolved in very dilute (10%) methyl alcohol and poured into a dilute solution of sodium carbonate. The crystalline precipitate was thoroughly washed with water and finally crystallised from dilute methyl alcohol in hexagonal plates melting at  $123^{\circ}$ . (Found: C=62.80; H=5.86.  $C_{12}H_{13}N_3S$  requires C=62.35; H=5.63 per cent.).

*Hydrolysis of 2-Keto-4-phenyl-2:3-dihydro-1:3-thiazole-isopropylene hydrazone: Formation of (IV).*—The hydrazone was boiled for a few minutes with concentrated hydrochloric acid and the solution was evaporated to dryness on the water bath. The residue was taken up with cold water, filtered and made alkaline with sodium carbonate. The resulting base was several times recrystallised from alcohol until the melting point reached  $168^{\circ}$ . (Found: N=22.03.  $C_9H_9N_3S$  requires N=21.99 per cent.). This compound was found to be identical with the product of hydrolysis of 2-keto-4-phenyl-2:3-dihydro-1:3-thiazole-acetyl hydrazone (*vide supra*).

The work is being continued with substituted thiosemicarbazides and monochloracetone, monochloracetal and esters of  $\alpha$ -halogenated acids

In conclusion, I take this opportunity of expressing my sincere thanks to Sir P. C. Rây for his keen interest throughout this investigation.

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# Varying Valency of Gold with respect to Mercaptanic Radicles.

## Part I.

BY

SIR PRAFULA CHANDRA RÂY.

In continuation of the study on the varying valency of platinum (Rây, T., 1923, 123, 133) that of gold has recently been undertaken. In the present communication have been described some bi-, ter-, quadri-, and quinque-valent gold compounds, showing thereby that the valency of gold like that of platinum is variable with respect to mercaptanic radicles.

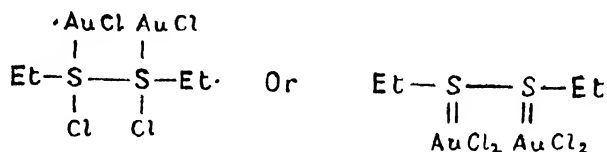
### *Bi-, Ter-, and Quadri-valent Gold.*

The starting mercaptanic derivative in this case also was diethyldisulphide, which on treatment with gold chloride (chlorauric acid), yielded a crystalline compound having the empirical formula  $\text{EtS} \cdot \text{AuCl}_2$ , to which may at first sight be assigned the graphic formula,

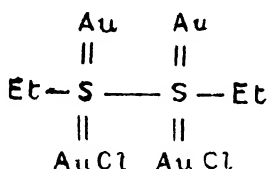
$\text{EtS} \cdot \text{Au} \begin{smallmatrix} \text{Cl} \\ < \\ \text{Cl} \end{smallmatrix}$  the gold behaving as tervalent. This

formula seemed to be unlikely as it would imply that during the reaction, the disulphide had undergone scission, thus:  $\text{EtS} - \begin{smallmatrix} \vdots \\ | \\ \vdots \end{smallmatrix} - \text{SEt}$ . Moreover, the product of the corresponding reaction with platinic chloride had the formula  $\text{Et}_3\text{S}_2\text{PtCl}$ , which has been shown to be a derivative of quinquevalent platinum and a sulphonium compound as well (*loc. cit.*). It was natural to suppose that the simple formula of the gold compound should be doubled, that is, it should be  $\text{Et}_3\text{S}_2 \cdot 2\text{AuCl}_2$ .

Determination of the molecular weight by the freezing point method has justified this conclusion. The compound can thus be represented as

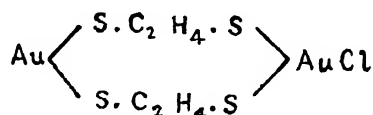


according as the gold is taken to function as bi- or quadri-valent. This constitutional formula of the chloromercaptide brings it into intimate relationship with the numerous sulphonium iodomercaptide derivatives, which the author has been studying during the last ten years (T., 1916, 109, 131, 603; 1917, 111, 101, etc.), where it is shown that the so-called "molecular compounds" of the type  $\text{R}_3\text{S}_2 \cdot \text{HgI}_2 \cdot \text{R}'\text{I}$  are in reality "atomic compounds" of the sulphonium type. Diethyldisulphide also furnishes another compound with gold chloride having the empirical formula  $\text{Et}_2\text{S}_2 \cdot \text{Au}_4\text{Cl}_2$ . Its constitution may be represented as



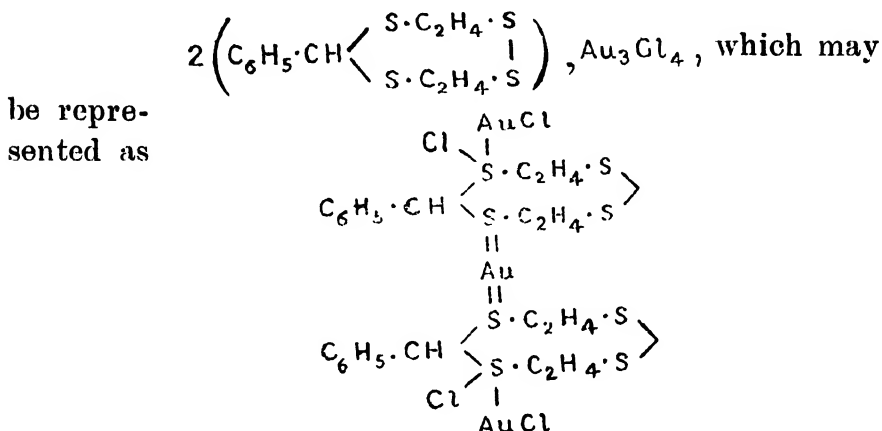
where sulphur is sexavalent and gold alternately bi- and ter-valent. Instances of chain compounds of sexavalent sulphur have already been given (Ray, T., 1919, 115, 548).

Bivalent gold evidently occurs in the compound  $\text{Au}_2\text{Cl}(\text{C}_2\text{H}_4\text{S}_2)_2$ —the product of the interaction of the monopotassium mercaptide (Ray, T., 1923, 123, 133) and gold chloride. It may be graphically represented as

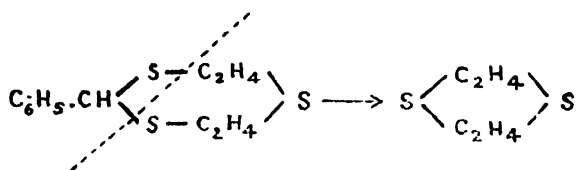


one atom of gold behaving as bi- and the other as ter-valent.

Benzaldiethylene tetrasulphide (RAY, T., 1924, 125, 1141) on treatment with gold chloride yielded the compound, conforming to the formula



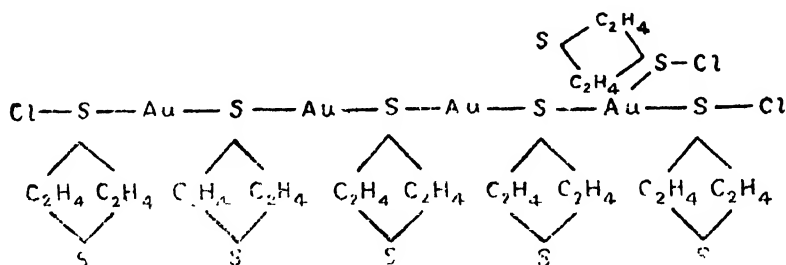
the gold functioning alternately as bi- and quadri-valent. When, however, benzaldiethylene trisulphide is similarly treated it has the structure broken up according to the scheme :



diethylene disulphide (1:4-dithian) being the degradation product. Evidently this scission takes place on account of the molecule being loaded with the heavy radicles of gold chloride. It has been shown in the previous communication (*loc. cit.*) that mercuric chloride and even a light radicle like methyl iodide brings about similar rupture. Representing the dithian molecule by A, the following compounds have been obtained : (a) 6A, Au<sub>4</sub>Cl<sub>3</sub> ;

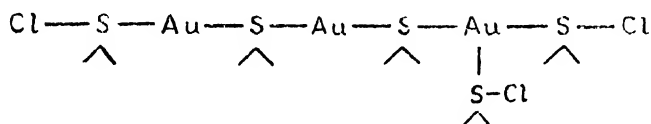
(b)  $5A, Au_3Cl_5$ ; (c)  $4A, Au_3Cl_4$ ; (d)  $4A, Au_3Cl_2$ ; (e)  $3A, Au_3Cl_2$  and (f)  $3A, Au_2Cl_2$ . In all these cases the temperature of the reaction varied as a rule from  $28^\circ$  to  $55^\circ$ . In one special case both the component solutions were heated to  $78^\circ$  and the resulting compound had the formula  $3(C_2H_4S_2)Au_3Cl_2$  (g), the 1:4-dithian molecule yielding a still simpler degradation product, namely, ethylene disulphide. It might be urged that there is the possibility of some of these compounds being contaminated with traces of reduced gold or of being mixtures. An alcoholic solution of gold chloride has, no doubt, been sometimes found to turn slightly turbid in course of a quarter of an hour or so, but the reactions involved were finished in less than a couple of minutes; moreover, within wide limits of temperature and concentration of the reacting components as also in both alcoholic and ethereal solutions the identical compound, *e.g.*, compound (a) has often been obtained. Hence the chances of their being mixtures are precluded.

The anomalous nature of these chlorides can be easily explained if the atoms of gold be taken as bi- and ter-valent respectively as in the instances cited above. Thus  $6A, Au_4Cl_3$  may be represented as



in which only one atom of sulphur of each of the dithian molecules becomes quadrivalent, the sulphur atoms at the extreme ends of the chain taking up the chlorine atoms, thus converting it into a sulphonium compound.

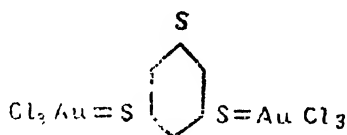
5A,  $\text{Au}_3\text{Cl}_5$  may from this point of view be looked upon as



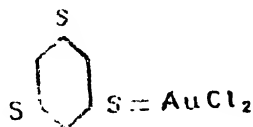
The other complex chlorides may similarly be graphically represented. It will thus be seen that the determining factor in the formation of these chlorides is the greater affinity of sulphur atoms for those of gold—the latter preferring to enter into combination with it and liberating chlorine (compare, Rây, T., 1923, 123, 131).

### *Quinquevalent Gold.*

Triethylene trisulphide (Rây, T., 1920, 117, 1090) by interaction with gold chloride has yielded two compounds, namely,  $(\text{C}_2\text{H}_4\text{S})_3 \cdot 2\text{AuCl}_3$  and  $(\text{C}_2\text{H}_4\text{S})_3 \cdot \text{AuCl}_2$ . The former may be represented as

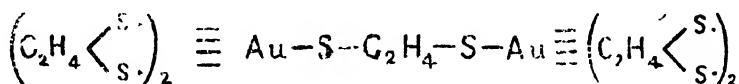


in which the gold functions as quinquevalent; similarly the second compound may be represented as



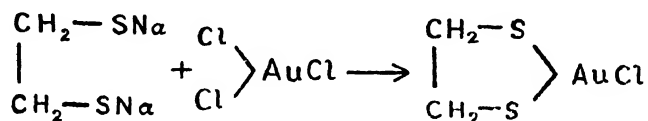
in which the gold functions as quadrivalent.

Direct proof of the quinquevalency of gold has also been obtained by the formation of the compound

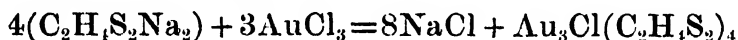




by the interaction of sodium dithioethylene glycol and gold chloride in acetone solution. The corresponding platinum compound has also been isolated. The disodium mercaptide was also treated with an ethereal solution of gold chloride. It was anticipated that the reaction would proceed as follows



but the compound actually obtained had the formula  $(\text{C}_2\text{H}_4\text{S}_2)_4 \cdot \text{Au}_3\text{Cl}$ . The reaction no doubt takes place according to the equation :



## EXPERIMENTAL.

### *Bi-, Ter-, and Quadri-valent Gold.*

*Action of Gold Chloride on Diethyl. Disulphide.*—The disulphide was treated with an excess of an aqueous solution of gold chloride and continuously stirred. At first a pasty deep yellow mass was obtained, which on ‘teasing’ with a rod solidified into a crystalline product. It was further purified by recrystallisation from boiling toluene. (Found: Au = 59.90; Cl = 21.39; S = 10.25.  $\text{C}_4\text{H}_{10}\text{S}_2\text{Au}_2\text{Cl}_4$  requires Au = 59.90; Cl = 21.58; S = 9.73 per cent.). The determination of the molecular weight by the freezing point method (in naphthalene) gave the result as 655, 666.8 and 670.3 respectively, the calculated molecular weight being 658. The compound when dissolved in naphthalene slowly deposits particles of gold; care should therefore be taken to finish the operation within half an hour. The determination of the molecular weight by the ebullioscopic method (in toluene) gave unsatisfactory

results for similar reasons. In fact, the separation of gold in this case is much more rapid. The compound slowly darkens on exposure to light due to separation of fine particles of gold. If, however, the above reaction be not allowed to go beyond the pasty stage and the mass extracted with ether, a portion goes into solution and the ethereal extract on spontaneous evaporation deposits a white amorphous powder, which conforms to the formula  $\text{Et}_2\text{S}_2, \text{Au}_4\text{Cl}_2$  (Found :  $\text{Au}=79.36$ ;  $\text{Cl}=7.45$ ;  $\text{S}=7.76$ . Theory requires  $\text{Au}=80.33$ ;  $\text{Cl}=7.24$ ;  $\text{S}=6.53$  per cent.). The crystalline insoluble residue was found to be identical with the previous compound.

*Action of Gold Chloride on Disodium Dithio-ethylene Glycol.*—To the dimercaptide suspended in ether was added an ethereal solution of gold chloride. Reaction at once commenced and the mixture was heated under reflux for 3-4 hours. A light brown precipitate put in an appearance. It was filtered and washed with water several times and dried in a vacuum over sulphuric acid. (Found :  $\text{Au}=59.90$ ;  $\text{S}=25.55$ ;  $\text{Cl}=3.75$ .  $\text{C}_8\text{H}_{16}\text{S}_2\text{Au}_3\text{Cl}$  requires  $\text{Au}=59.42$ ;  $\text{S}=25.74$  and  $\text{Cl}=3.57$  per cent.).

*Action of Gold Chloride on Monopotassium Dithioethylene Glycol.*—In the case of platinum it has already been found that the particular valency which the metal might take up depends upon the concentration as also the temperature of the participants (Ray, T., 1923, 123, 133). Similar *modus operandi* was adopted in this case. 12 c.c. of gold chlorine solution (1 c.c. = 0.0260 gm. Au) were added to 0.5500 gm. of the potassium salt of dithioethylene glycol dissolved in 15 c.c. of water at  $5^\circ$ ,  $28^\circ$ ,  $65^\circ$  and  $80^\circ$  in different preparations. A brown precipitate was formed in each case. It was washed with water, alcohol and ether and dried in a vacuum. All the preparations were found to be identical in composition. (Found :  $\text{Au}=62.23$ ;

Cl=4.65; S=21.18.  $C_4H_8S_4Au_2Cl$  requires Au=62.39; Cl=5.62 and S=20.27 per cent.).

*Action of Gold Chloride on Benzaldithylene Tetrasulphide.*—An alcoholic solution of gold chloride was added in a thin stream under vigorous agitation to an ethereal solution of the sulphide. A flocculent reddish precipitate was formed. It was washed with ether and dried in a vacuum. It had the formula  $2[C_6H_5CHS_4(C_2H_4)_2], Au_3Cl_4, (C_2H_5)_2O$ .\* (Found: Au=42.40; Cl=10.53; S=19.70.  $C_{26}H_{38}OS_8Au_3Cl_4$  requires Au=43.62; Cl=10.48; S=18.89 per cent.). The same compound was also obtained when both the components were mixed in ethereal solution. From the filtrate of the latter again a further quantity of a precipitate with identical composition was obtained.

*Action of Gold Chloride on Benzaldithylene Trisulphide.*—(a) *Expt. 1.*—0.1940 gm. of the sulphide was dissolved in 5 c.c. of alcohol. To it was added 2 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0510 gm. Au). The reaction was carried out at 55°. *Expt. 2.*—The same quantity of the sulphide was dissolved in 10 c.c. of alcohol and to it was added 3 c.c. of gold chloride of the same strength as above. The temperature of the reaction was 40°. *Expt. 3.*—The same quantity of the trisulphide was this time dissolved in 15 c.c. of alcohol and to it was added 3 c.c. of gold chloride. The temperature of the reaction was 30°. *Expt. 4.*—0.1730 gm. of the sulphide was dissolved in 4 c.c. of alcohol and to it was added 8 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0155 gm.

\* In these and the compounds of gold and platinum to be subsequently described a molecule or more of ether or alcohol of combination, as the case may be, often occurs. (Compare Rây, T, 1924, 125, 1143) The filtrate from the product of reaction of benzaldithylene trisulphide and platinum chloride (*loc. cit.*) in alcohol deposited a compound of the formula  $C_{11}H_{14}S_3 \cdot PtCl_2 \cdot 3EtOH$ . (Found: Pt=30.45; Cl=9.85; C=31.26; H=4.73. Theory requires Pt=30.40; Cl=10.06; C=31.48; H=4.93 per cent.)

Au) at  $28^{\circ}$ . *Expt. 5.*—0.2160 gm. of the sulphide was dissolved in 5 c.c. of alcohol and to it was added 10 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0155 gm. Au). The temperature of the reaction was  $50^{\circ}$ . In each of these cases the compounds obtained had identical composition. The formation of one and the same compound within wide limits of temperature and concentration also precludes the possibility of their being any mixtures. It conformed to the formula  $6[(C_2H_4)_2S_2], Au_4Cl_3$ . (Found: Au=49.06; Cl=6.78; S=23.52.  $C_{21}H_{18}S_{12}, Au_4Cl_3$  requires Au=48.79; Cl=6.79; S=23.77 per cent.).

(b) 0.2174 gm. of the trisulphide was dissolved in 5 c.c. of ether and cooled with ice-water. To it was added an excess of gold chloride in ether (1 c.c.=0.0273 gm. Au) under vigorous agitation. The brown precipitate was washed with ether and dried in a vacuum. It conformed to the formula  $5[(C_2H_4)_2S_2], Au_3Cl_5, 1\frac{1}{2}(C_2H_5)_2O$ . (Found: Au=42.00; Cl=12.18. Theory requires Au=42.03; Cl=12.62 per cent.).

(c) In this experiment the components were dissolved in ethereal solution and were mixed in indefinite proportions. The compound had the formula  $4[(C_2H_4)_2S_2], Au_3Cl_4, \frac{1}{2}(C_2H_5)_2O$ . (Found: Au=47.61; Cl=11.42. Theory requires Au=47.38; Cl=11.36 per cent.).

(d) 0.1300 gm. of the sulphide was dissolved in 3 c.c. of alcohol and heated to about  $72^{\circ}$ . To it was added 10 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0155 gm. Au). The compound obtained had the formula  $4[(C_2H_4)_2S_2], Au_3Cl_2$ . (Found: Au=52.17; Cl=6.35; S=22.43. Theory requires Au=51.75; Cl=6.22 and S=22.41 per cent.).

(e) 0.4991 gm. of the sulphide was dissolved in alcohol. To it was added drop by drop under constant agitation 1 c.c. of an alcoholic solution of gold chloride (1 c.c.=0.0623 gm. Au). A purple precipitate was obtained. It

was washed first with benzene and then with alcohol and dried in a vacuum. Under the microscope it revealed a brown, spongy texture but no gold particles. It conformed to the formula  $3[(C_2H_4)_2S_2], Au_3Cl_2, C_2H_5OH$ . (Found:  $Au=55.76$ ;  $Cl=6.98$ . Theory requires  $Au=55.34$ ;  $Cl=6.65$  per cent.).

(f) (*Expt. 1*).— $0.3582$  gm. of the sulphide was dissolved in 25 c.c. of alcohol and heated on the waterbath to  $60^\circ$ . To it was added an excess of an alcoholic solution of gold chloride (1 c.c.= $0.1066$  gm Au) all at once and agitated on the waterbath between  $60-70^\circ$ . (*Expt. 2*).— $0.2750$  gm. of the sulphide was dissolved in 10 c.c. of alcohol and heated to  $40-50^\circ$ . To it was added  $6.5$  c.c. of an alcoholic solution of gold chloride (1 c.c.= $0.0425$  gm. Au) all at once and vigorously agitated. In both these preparations the compounds had identical composition and conformed to the formula  $3[(C_2H_4)_2S_2], Au_2Cl_2, C_2H_5OH$ . (Found:  $Au=45.61, 45.64$ ;  $Cl=8.43, 8.74$ ;  $S=23.22, 23.80$ . Theory requires  $Au=45.24$ ;  $Cl=8.15$ ;  $S=22.04$  per cent.).

(g)  $0.4110$  gm. of the sulphide was dissolved in 30 c.c. of alcohol and heated on the waterbath and to it was added  $6.5$  c.c. of gold chloride in alcohol (1 c.c.= $0.0425$  gm. Au) and again heated on the waterbath for a few minutes more. The product agreed with the formula  $3[(C_2H_4)_2S_2], Au_3Cl_2, C_2H_5OH$ . (Found:  $Au=60.34$ ;  $Cl=7.27$ ;  $S=19.08$ . Theory requires  $Au=60.06$ ;  $Cl=7.22$ ; and  $S=19.51$  per cent.).

### *Quinquevalent Gold.*

*Disodium Dithioethylene Glycol.*—To an ethereal solution of dithioethylene glycol, very finely divided metallic sodium was added, care being taken to exclude moisture. Slow evolution of hydrogen took place and a fine

crystalline powder of the dimercaptide was formed. (Found: Na=32·71.  $C_2H_4S_2Na_2$  requires Na=33·34 per cent.).

*Action of Gold Chloride on Disodium Dithioethylene glycol.*—The dimercaptide was suspended in acetone and an acetone solution of gold chloride was added. The mixture was digested on the water bath for about an hour. The product had the formula  $C_{10}H_{20}S_{10}Au_2$ . (Found: Au=47·38, S=36·19,\* C=14·05. Theory requires Au=46·13, S=37·50, C=14·00 per cent.).

*Action of Gold Chloride on Triethylene Trisulphide.*—Alcoholic solutions of the components were mixed together. An orange-colored precipitate was immediately formed. It conformed to the formula  $(C_2H_4S)_3 \cdot 2AuCl_3$ . (Found: Au=50·90; Cl=26·39; S=11·03.  $C_6H_{12}S_3Au_2Cl_6$  requires Au=50·06; Cl=27·06; S=12·20 per cent.). The alcoholic filtrate containing an excess of gold chloride deposited on spontaneous evaporation, a crop of white crystals of the formula  $(C_2H_4S)_3 \cdot AuCl_2$ . (Found: Au=44·00; Cl=15·27; S=20·73.  $C_6H_{12}S_3AuCl_2$  requires Au=43·97; Cl=15·87; S=21·43 per cent.).

In conclusion, I avail myself of this opportunity to express my cordial thanks to Messrs. Indu Bhusan Sen Gupta and Khitish Chandra Rây for the patience and skill with which they conducted the experimental part of this investigation.

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UNIVERSITY OF CALCUTTA.

[Received May 29, 24]

\* The estimation was effected by fusion with  $Na_2CO_3$  and  $KNO_3$ . Traces of sulphur are converted into sulphonio acids owing to the presence of the radicle  $O_3H$ , and hence the percentage of sulphur comes out slightly low. (Compare Rây, T., 1920, 117, 1091).

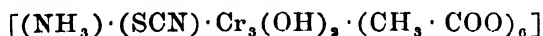


# Complex Chromium Ammonium Compounds

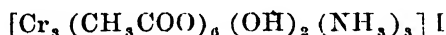
BY

PRIYADARANJAN RÂY AND PULIN BEHARI SARKAR.

This paper forms a part of a systematic investigation on the action of ammonium thiosulphate and ammonia upon chromium and cobalt hydroxides. The action of concentrated ammonia and ammonium thiosulphate upon chromium hydroxide has led to the production of two interesting trinuclear chromium ammonium compounds in which the chromium atoms are linked to one another by single bridges through hydroxyl groups. The preparation, description and the establishment of the constitution of these compounds form the subject of the present paper. Examples of trinuclear cobalt compounds with definite constitution are known. But in the case of chromium, though we are familiar with binuclear compounds like rhodochromium and erythrochromium salts, no trinuclear-ammino-compound of definite constitution has yet been described. Werner (Ber., 1908, 41, 3447) and Weinland and Gussmann (Zeit. anorg. Chem., 1910, 67, 167), however, have described a number of compounds with organic fatty acids which contain three chromium atoms in a molecule. A glance at the formulæ of the compounds, namely, monammino-hexacetato-diol-trichromirhodanat



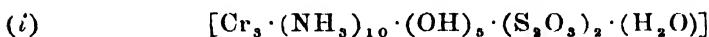
and hexa-acetato-dihydroxy-triammino-trichromi-iodide



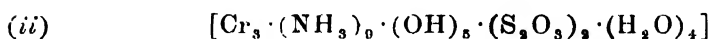
which may be regarded representative of the series, will make it clear. Both the authors have, however, attempted



to clear their constitution, but their views still leave two of the chromium atoms co-ordinatively unsaturated. But these two compounds prepared by the action of ammonium thiosulphate and ammonia upon chromium hydroxide possess the following composition—

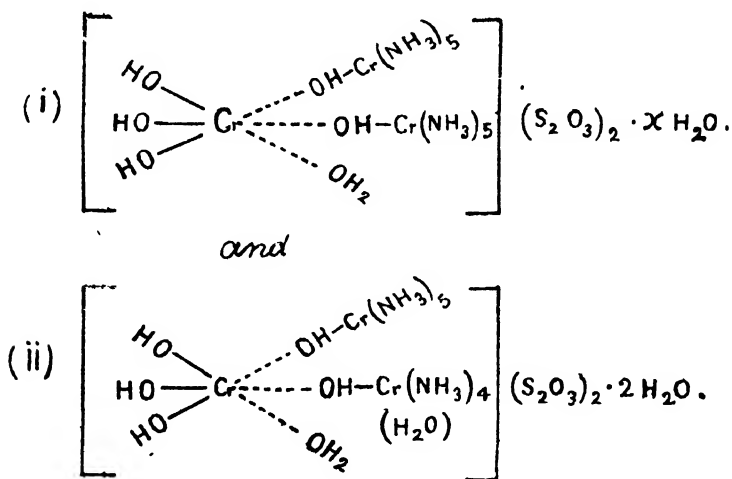


Decammin-monaquo-trihydroxy-diol-trichromium thio-  
sulphate and



Enneammin-diaquo-trihydroxy-diol-trichromium thiosulphate.

Definite constitution based on Werner's theory can be readily attributed to them; and these have been confirmed by their general behaviour and properties. Their constitutions are represented by the following formulæ:—



Both of them are trinuclear compounds with single bridges. The second is evidently formed from the first by the displacement of one molecule of ammonia by a molecule of water.

## EXPERIMENTAL.

*Preparation of the decammin-monaquo-trihydroxy diol-trichromium thiosulphate.*—Pure chromium hydroxide prepared from 50 grams of chrome alum was mixed with 50 gms. of ammonium thiosulphate dissolved in a small quantity of water; the mixture was then placed in a strong or pressure bottle and saturated with ammonia gas for several hours till a dark violet solution was obtained and the undissolved chromium hydroxide assumed a violet colour. The mixture was then kept in the dark for some days after which it was filtered. The filtrate was then cooled by ice and treated further with a strong current of ammonia gas. After half an hour or so a dark viscous oily liquid separated out at the bottom. The supernatant solution was then decanted into another flask. The oily liquid was first washed several times with a mixture of alcohol and liquor ammonia (1 : 3) to remove any excess of ammonium thiosulphate, then with absolute alcohol when the oil crystallised completely. The crystals were filtered on the pump at once and washed with absolute alcohol and then in some cases with anhydrous ether. They were dried on the pump by strong suction and removed into weighing bottle at once. The crystals could not be dried in a desiccator as the compound would decompose gradually at atmospheric pressure with loss of ammonia; nor was it found possible to dry the crystals in an atmosphere of dry ammonia.

From the mother liquor another crop was obtained by the careful addition of alcohol, an oil separated out which was washed, crystallised and treated as described above. The final mother liquor on exposure to air for a day or two slowly gave a deposit consisting mostly of violet chromium hydroxide mixed with ammonia and a little ammonium thiosulphate. The yield amounted to only 2.25 gms.

*Properties.*—The crystals were reddish violet, very unstable, readily losing ammonia, extremely hygroscopic and turned into oily liquid by the absorption of moisture. With water a dark oil was formed which slowly passed into a violet-coloured solution and decomposed readily with precipitation of chromium hydroxide. It dissolved slowly in strong ammonia to a clear solution and was decomposed readily by caustic alkalies with evolution of ammonia and separation of chromium hydroxide. With dilute acids sulphur dioxide was evolved and sulphur was precipitated. The substance itself was basic to litmus. With moist silver oxide and water the whole of the thiosulphate was removed and the filtrate was strongly basic. Barium chloride solution also removed the whole of the thiosulphate as barium thiosulphate and a violet solution of the corresponding chloride, which was fairly stable, was obtained. This solution was basic to litmus and gave the following reactions.

1. Potassium ferrocyanide solution gave at first a flocculent and then a light blue-violet crystalline precipitate.

2. Potassium ferricyanide solution gave at first a flocculent and then a crystalline pink-coloured precipitate.

3. Mercuric chloride solution gave a light violet-blue flocculent precipitate.

4. Potassium chromate, after the removal of barium by ammonium sulphate, gave no precipitate but potassium dichromate gave a yellowish brown precipitate.

5. Solid potassium iodide gave a light blue gelatinous precipitate.

6. On evaporation with concentrated hydrochloric acid chromic chloride was formed in solution and the characteristic red-violet crystals of chloropentammin chloride separated out.

Results of analysis :—

I. Sample precipitated by alcohol.

0·4832 gm.	gave 0·1277 gm. of $\text{Cr}_2\text{O}_3$ ,	$\text{Cr}=18\cdot11\%$
„ „ „	0·5214 gm of $\text{BaSO}_4$ ,	$\text{S}=14\cdot81\%$
		or $\text{S}_2\text{O}_3=25\cdot92\%$
0·3596 „ „	0·0697 gm. of $\text{NH}_3$ ,	$\text{NH}_3=19\cdot37\%$
Hence	$\text{Cr} : \text{S}_2\text{O}_3 : \text{NH}_3=3:2 : 10.$	

II. Sample precipitated by continuous passage of ammonia,

0·1458 gm.	gave 0·0422 gm of $\text{Cr}_2\text{O}_3$ ,	$\text{Cr}=19\cdot8\%$
„ „ „	0·1653 gm. of $\text{BaSO}_4$ ,	$\text{S}=15\cdot63\%$
		or $\text{S}_2\text{O}_3=27\cdot35\%$
0·0904 gm. „	0·0190 gm. of $\text{NH}_3$ ,	$\text{NH}_3=21\cdot0\%$
Hence	$\text{Cr}:\text{S}_2\text{O}_3:\text{NH}_3=3:2:10$	

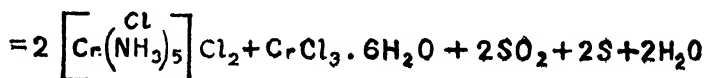
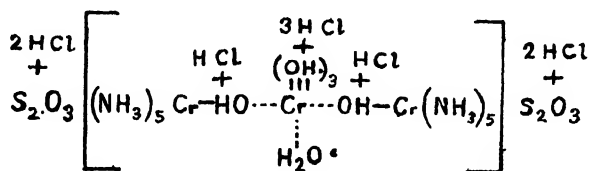
III. Sample precipitated by 30% alcoholic ammonia from the mother liquor of sample II and washed finally with anhydrous ether.

0·2556 gm.	gave 0·0805 gm. of $\text{Cr}_2\text{O}_3$ ,	$\text{Cr}=21\cdot55\%$
„ „ „	0·3500 gm. of $\text{BaSO}_4$ ,	$\text{S}=18\cdot8\%$
		or $\text{S}_2\text{O}_3=32\cdot9\%$
0·2671 gm. „	0·06207 „ of $\text{NH}_3$ ,	$\text{NH}_3=23\cdot24\%$
Hence	$\text{Cr} : \text{S}_2\text{O}_3 : \text{NH}_3=3 : 2 : 10.$	

The atomic ratio in all these samples is, therefore, quite constant, the percentage amount only varied due to the change in the extent of hydration.

*Constitution.*—As the salt decomposed readily in contact with water no conductivity measurement was possible. The action of silver oxide and barium chloride indicated that both the thiosulphate radicles were in the outer zone. The action of concentrated hydrochloric acid indicated the presence of pentammine. In the light of these facts the compound should be represented by the constitutional formula No. (i), page 92.

The action of strong hydrochloric acid can then be represented as follows :—



*Preparation of Enneammin-diaquo-trihydroxy-diol-trichromium thiosulphate.*—Chromium hydroxide from 50 gms. of chrome alum prepared and purified as described before was mixed with 50 gms. of ammonium thiosulphate dissolved in a small quantity of water; the mixture was placed in a pressure bottle and saturated with ammonia in the cold at  $0^\circ \text{C}$ ; the bottle was then tightly closed and kept in the dark for 3-4 months. After this time pink-violet crystals separated from the solution and these remained mixed with the undissolved chromium hydroxide. The mass was then agitated with water and the chromium hydroxide removed as suspension by repeated washing. The washing was repeated several times followed by gentle grinding with water. The crystals were afterwards obtained in a fairly pure condition. These were then washed with alcohol and dried in vacuum.

*Properties.*—It consisted of pink-violet crystals, insoluble in water, slightly alkaline to litmus and quite stable in the dry state. Barium chloride removed the whole of the thiosulphate. Lead acetate and silver nitrate behaved similarly. Concentrated hydrochloric acid gave chloropentammine chloride in small quantities with chromic chloride and an evolution of sulphur dioxide and precipitation of sulphur took place. The solution

obtained by decomposition with barium chloride decomposed slowly in light giving precipitates of chromium hydroxide. A freshly prepared solution obtained by decomposition with barium chloride gave the following reactions :—

1. Potassium ferrocyanide solution gave at first a flocculent then a very light pink crystalline precipitate.

2. Potassium ferricyanide solution gave on warming a dull brown precipitate.

3. Mercuric chloride solution gave a voluminous pink precipitate.

4. Potassium chromate solution, after the removal of barium with ammonium sulphate, gave no precipitate while potassium dichromate gave a light brown crystalline precipitate.

5. Solid potassium iodide gave a heavy pink crystalline precipitate.

### *Analysis and Composition.*

1. 0.1474 gm. of the substance gave 0.0501 gm. of  $\text{Cr}_2\text{O}_3$  :  
 $\text{Cr} = 23.2\%$   
       "      "      "      "      0.2057 gm. of  $\text{BaSO}_4$ ,  
 $\text{S} = 19.1\%$   
   0.0570 "      "      "      "      0.0130 gm. of  $\text{NH}_3$ ,  
 $\text{NH}_3 = 22.75\%$   
   0.0924 "      "      "      "      0.0202 gm. of  $\text{NH}_3$ ,  
 $\text{NH}_3 = 21.87\%$
- II. 0.2344 gm. of the substance gave 0.0794 gm. of  $\text{Cr}_2\text{O}_3$ ,  
 $\text{Cr} = 23.00\%$   
       "      "      "      "      0.3163 gm. of  $\text{BaSO}_4$ ,  
 $\text{S} = 18.55\%$

$[\text{Cr}_2(\text{NH}_3)_6, (\text{OH})_6 \cdot (\text{S}_2\text{O}_3)_2, (\text{H}_2\text{O})_4]$  requires

$\text{Cr} = 22.75\%$ ,     $\text{S} = 18.66\%$ ,     $\text{NH}_3 = 22.3\%$  per cent.

*Constitution.*—The substance was basic to litmus hence it was inferred to be a hydroxo compound. The action of strong hydrochloric acid indicated that it contained a



. As the compounds are either almost insoluble or unstable in water, their constitution could not be confirmed by physical methods.

Our best thanks are due to Prof. Sir P. C. Rây for the kind interest he has taken in the work.

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# **The Condensation of Resorcinoland a few other Aromatic Hydroxy Compounds with some Acids, Esters, Lactones and Lactams.**

BY

RAJENDRA NATH SEN

AND

SARBANI SAHAYA GUHA SIRCAR.

A considerable amount of work has been done on the condensation of phenols with the anhydrides of polybasic organic acids, by Baeyer and a host of other investigators.<sup>1</sup>

The very wide application of the reaction between phenols and acid anhydrides has established beyond doubt peculiar reactivity of the carbonyl group of the acid anhydride in giving rise to phthalein-like bodies.

A slightly different type of acid anhydride is *o*-sulpho benzoic anhydride, which was also observed by Schon to react with phenols in the same manner as phthalic anhydride (Amer. Chem. J., 1898, 20, 257). The 'sulpham' of this anhydride (benzoic sulphimide), or 'saccharin,' was also found to behave similarly. (Monnet and Koetschet, Bull. Soc. Chim., 1897, 17 (ii), 690; also Dutt, T. 1922, 121, 2389).

<sup>1</sup> Baeyer (Ber., 1871, 4, 658); Baeyer and Caro (Ber., 1875, 7, 968); Lunge and Burckhardt (Ber., 1884, 17, 1598; Ber. 18, 2864. Silberrad, Proc. 1908, 209; Nencki and Sieber (1881, Ai, 671); (1881, A-1, 591 and 811), J. Pr. Chem. [2], 28, 147-156 and 537-550. Succino-rhodamine Ber. 23, R. 811), in more recent years, Quinolineins (Ghosh, 1919, T. 1104); Citraconeins, Shri Krishna and Pope (1921, T. 289); Camphoreins (Sircar and Dutt, 1922, T. 1283; Shri Krishna, T. 253; and Singh, Rai and Lal T. 1421 in the same year); Phenyl-succineins, Lapworth and MacRae (1922, T. 2722); Diphenesins, Dutt (1923, T. 225).

The last mentioned example suggested a study of the reactivity of the carbonyl group in configurations other than that of anhydrides. Besides the case of 'saccharin,' there are a few other instances of such in the literature. Thus, some monobasic organic acids were found by Cohn to react with resorcinol to give rise to what are known as the 'benzeins,' which are very much analogous to phthaleins (Cohn, Ber. 1892, 24, 2064). Another instance of the reactivity of the carbonyl group in giving rise to phthalein-like products, is found in Sri Krishna's work on the condensation of the lactone, coumarin with phenol and resorcin (1921, T. 1420).

The present work has for its object the further study of the reactivity of the carbonyl group specially in configurations not hitherto investigated, in respect of condensation with resorcinol and similar other aromatic hydroxy compounds. It seems that the condensation of this type between acids and phenols has not been studied sufficiently thoroughly so as to establish the generality of the reaction, while the study of the reactivity of esters, lactones and lactams (all of which contain the reactive carbonyl group), presents an almost untrodden ground.

With this object in view, typical acids of the aliphatic, aromatic and heterocyclic series, have been taken for investigation and found to give phthalein-like products with resorcin, pyrogallol, etc.

The behaviour of esters has also been examined to determine if they were more or less reactive than the acids, and it has been found that, as a rule, the esters react with greater ease than the acids from which they are derived.

As the reactivity of lactones was only indicated by Sri Krishna's work on coumarin (*loc. cit.*), more work on this line seemed desirable to establish the generality of the reaction.

The lactam, isatin has also been examined with the same object, it being found that the lactamic, or the  $\alpha$ -carbonyl group may also be made to react with phenol, resorcinol, etc., to give products analogous to phthaleins.

A much more interesting case for study was found in the investigation whether both the carbonyl groups of the anhydrides of dibasic acids can be made to react either simultaneously or successively. This part of the work presents an entirely new aspect of the question, not having been hitherto investigated by previous workers. The present work in this direction goes to show that the reaction does not, under ordinary circumstances, take place with both the carbonyl groups simultaneously, though it is possible to make them react successively, with the same or different phenols, with good yield. Under more drastic conditions, *viz.*, heating longer at higher temperature, with larger quantity of condensing agent, it is also possible to make both the carbonyl groups of phthalic anhydride react simultaneously with resorcinol, though the yield of the desired product is rather small.

The results of the present investigation are briefly as follows:—

In the acid series, two hydroxy acids (salicylic and gallic) have been found to give fluoresceins when heated with resorcin in presence of zinc chloride (powdered and anhydrous), in a current of dry hydrochloric acid to 180-200°C.

Salicylic acid has been found to condense with pyrogallol as well, to give a product non-fluorescent in alkalies or organic solvents.

An amino acid, *viz.*, anthranilic acid, has been condensed with resorcin and diethyl-*m*-amido-phenol and found to give a benzein in the one case, and a rhodamine in the other. The *o*-amino-resorcinol benzein thus obtained, is found to have a fluorescence of the same kind as that of

the *o*-hydroxy compound derived from salicylic acid. Both give orange-green fluorescence in alkaline solutions which however changes to bluish-red on standing,—the change in the case of the amino-benzein taking place with greater ease. The rhodamine gives red solutions with greenfluorescence in acids and organic solvents. The effect of the substitution of amino group for hydroxyl group in the benzeins, is therefore not very marked. The presence of free amino group in the final product is proved by the isocyanide reaction and by the action of nitrous acid.

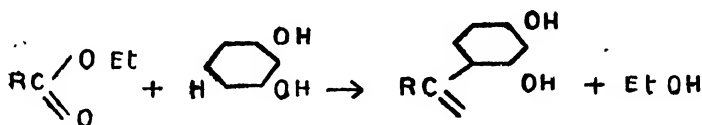
An aliphatic acid, *viz.*, stearic acid, has also been condensed with resorcin, yielding a fluorescein. Unlike the other products this is found to dissolve in benzene and less readily in ether. The compound is found to have only a moderate affinity for animal fibres. The fluorescence is also a little subdued.

Pyromucic acid, a heterocyclic acid, also gives a fluorescein with resorcin. The compound has been obtained by heating mucic acid and resorcin with zinc chloride in a current of dry hydrochloric acid. In alkaline solution the fluorescence changes from a greenish to a bluish tone on standing.

It is interesting to note that the bromine-content in the bromo derivatives of the above compounds, seems to vary according to the nature of the compound, for some of the compounds give tetra- (those derived from benzoic and salicylic acids), and some di-bromo derivatives (those from gallic and anthranilic acids), when the bromination is effected under similar conditions without taking any precautions. This is in agreement with Cohn's observations regarding similar compounds previously mentioned (*loc. cit.*).

Two esters, those of benzoic and salicylic acids, have also been examined. It is found that the reaction

between them and resorcinol, pyrogallol, etc., takes place with a greater readiness than in the case of corresponding acids. The yields are much better. The greater facility of the reaction in the case of the esters, may be plausibly explained by assuming that the first stage of the reaction consists in the elimination of a mol. of alcohol instead of a mol. of water as in the previous case,



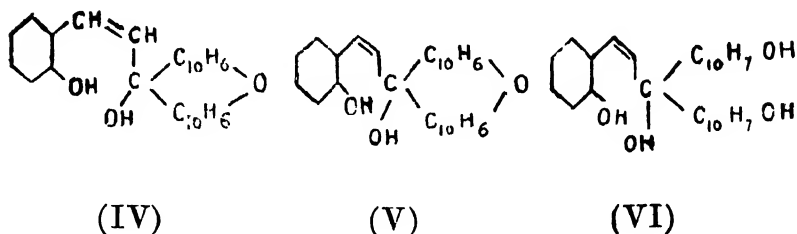
while the subsequent stages are the same in both the cases. The elimination of alcohol may be supposed to take place with greater ease than that of water.

In the study of condensation of lactones, the present work has been chiefly done on coumarin, in extension of previous work. It is found that it also gives a rhodamine (not previously prepared) with diethyl-*m*-amidophenol, which has properties analogous to true rhodamines, both in colour, dyeing properties, and solubility.

$\alpha$ - and  $\beta$ -naphthols have also been condensed with coumarin, giving rise to phthalein-like bodies. The  $\beta$ -naphthol compound is found to dissolve in caustic soda with strong green fluorescence. The ready solubility in alkali is explained by the non-closure of the lactone ring in the final product. This assumption is confirmed by analytical data which correspond to the structure (IV).

The  $\alpha$ -naphthol compound, which was found extremely difficult to purify owing to tar-formation, is also slightly fluorescent in caustic soda solution, due no doubt, to partial *o*-condensation giving a fluorane-like substance, (V).

The main product being  $\alpha$ -naphthol coumaren (VI)



Complete separation could not be effected as both the products dissolve in the same solvents.

Pyrogallol has also been found to condense with coumarin to give a non-fluorescent substance of "gallein-" like nature.

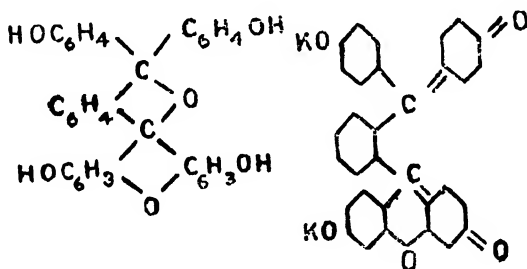
An observation that repeatedly engages the attention in the study of these condensations, is the peculiar behaviour of compounds in which pyrogallol is the second or phenolic component. It is found that all such compounds are non-fluorescent in alkaline solutions as well as in organic solvents, though the only difference between them and the resorcinol derivatives consists in the presence of additional hydroxyl groups in the former, in the *o*-positions to the pyrone-oxygen atom.

Coming at last to the study of the reactivity of both the carbonyl groups in the anhydride of dibasic acids (phthalic anhydride being chosen in the present case), the following observations were made in the course of the present work.

It was found that on heating the anhydride (one mol.) with four mols. of resorcin to 220°C with zinc chloride in a current of dry hydrochloric acid, no other product than fluorescein was obtained. Phenol-phthalein (a compound in which one of the carbonyl groups has already been acted upon), was next heated with resorcin and zinc chloride in a current of dry hydrochloric acid to 180-200°C. Curiously enough, it was found that fluorescein was

formed under the circumstances as previously observed by Meyer and Pfotenbauer (Ber., 1905, 38, 3958).

Phenol-phthalein was then heated with an excess of resorcin (about 2.5 mols.) with a larger quantity of zinc chloride in a current of dry hydrochloric acid to 220°C, for five hours. Under these conditions the desired condensation was effected, and on purification the product was found to be an extremely interesting compound in which both the carbonyl groups of the anhydride were acted upon, the first with phenol, and the second with resorcinol mols. It is thus a compound which contains both a phenol-phthalein and a fluorescein component. The constitution (VII) is given to this compound.



(VII)

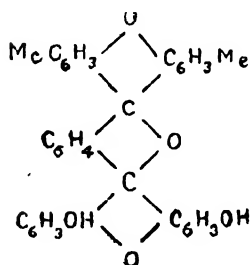
(VIII)

It dissolves in alkalis and organic solvents with an intense green fluorescence in no way inferior to that of fluorescein itself. It gives a tetrabromo derivative corresponding to eosin and a di-potassium salt, formulated as in (VIII). The compound is thus doubly quinonoid. The intensity of the colour and fluorescence is no doubt ascribable to 'double symmetric tautomerism,' which it is obviously capable of exhibiting.

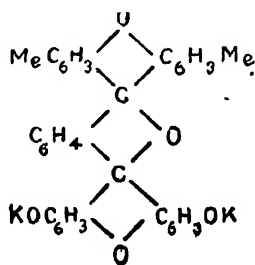
The compound may also be regarded as being formed by the condensation of one of the carbonyl groups of phthalic acid with two mols. of phenol, and of the other carbonyl group with two mols. of resorcinol.



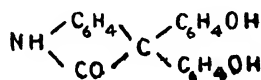
To confirm the reactivity of the second carbonyl group of phthaleins, *p*-cresol-phthalein anhydride was prepared according to Drewsen (A. 212, 340-47) by heating phthalic anhydride (one mol.) and *p*-cresol (two mols.) with conc. sulphuric acid. The compound was chosen in preference to *o*-phenol-phthalein anhydride, as the latter is difficult to prepare in any quantity. The anhydride chosen is interesting also in having a pyrone-ring already formed in the molecule. The product of condensation of the anhydride with resorcin, is found to dissolve with less ease in alkalies and to give a solution, the fluorescence of which is less bright than that of fluorescein, being more red and less orange on dilution than fluorescein. The difference is no doubt ascribable to the increased complexity of the mol., and to the presence of methyl groups in *p*-positions to the pyrone-oxygen. It is given the constitution (IX), the potassium salt having the constitution (X).



(IX)



(X)



(XI)

Fluorescein itself when heated with excess of (3 mols.) resorcin, with excess of zinc chloride in a current of dry hydrochloric acid to 230-40°C for 6 to 7 hours, was found to give a product, which unlike fluorescein, is insoluble in sodium carbonate and precipitated by carbon dioxide from solutions in caustic soda. On purification, this gives a solution in caustic soda, the fluorescence of which is somewhat subdued, and much less bright than that of

fluorescein itself. Analytical results agree with the compound expected.

The last three condensations may be classed with those of the lactones, as the first components in these reactions are compounds of the lactone type. Looked at from this point of view it is hardly surprising that these condensations should be possible, though it must be admitted that they take place under conditions more drastic than in any other case hitherto studied. The heaviness and complexity of the molecules sufficiently explain the difference.

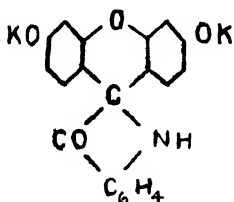
In the lactam series, only one lactam, *viz.*, isatin, has been studied. It was found by Baeyer and Lazarus (Ber. 18, 2637-43), to condense with phenol, toluene, anisole and di-methylaniline in presence of conc. sulphuric acid at ordinary temperatures, the condensation taking place with the  $\beta$ -carbonyl group of isatin.

In connection with the present investigation, phenol and isatin were *heated* with conc. sulphuric acid to 120-30°C for 6 to 7 hours, but the product was identical with "phenol-isatin" obtained by Baeyer to which he gave the constitution (XI).

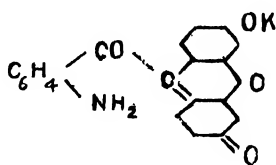
In the present work, isatin has also been condensed with phenol in the presence of zinc chloride at 180-90°C. The product is found to dissolve in caustic soda with red colour much deeper than that of alkaline solutions of 'phenol-isatin,' and produces no colour effect in alkaline solution by the addition of potassium ferrocyanide while 'phenol-isatin,' under similar conditions gives a violet colour. The difference between the two compounds is ascribed to the condensations having taken place with the  $\alpha$ -carbonyl group in one case and with the  $\beta$ -carbonyl group in the other.

Isatin has also been found to condense with resorcin, in the presence of zinc chloride in a current of dry hydrochloric acid giving a product analogous to fluorescein.

Diethyl-*m*-amidophenol also condenses to give a rhodamine. The resorcin compound gives a di-potassium salt which probably has the constitution (XII)



(XII)



(XIII)

In this compound, it is interesting to find that though no quinonoid form is possible under ordinary conditions, yet it is fluorescent and coloured. The fluorescence is however slight in alkaline solution, though marked in conc. sulphuric acid solution. By assuming that the lactam-ring is broken by hydrolysis, quinonoid form (XIII) becomes possible. This however does not explain the existence of the di-potassium salt.

The following further experiments have been made to establish whether the  $\alpha$ - or the  $\beta$ - carbonyl group of isatin reacted in these compounds.

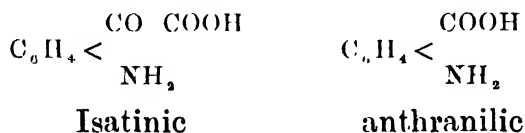
(1) Both isatin, and 'phenol-isatin,' as well as the present products liberate nitrogen with nitrous acid.

(2) With chloroform and alcoholic potash isatin and also 'phenol-isatin' are unaffected. The present products react vigorously with the reagents, and the smell of isocyanide slowly develops in the mixture on standing. This may be due to the breach in the lactam ring by hydrolysis, and formation of a free amido group.

(3) Both 'phenol-isatin' and the present products are insoluble in sodium carbonate and precipitated by carbon-dioxide from solution in caustic soda probably because under ordinary conditions the lactam ring is unaffected.

The difference in behaviour in isocyanide-reaction may be ascribed to the fact that while in 'phenol-isatin' the

$\beta$ -carbonyl group of isatin was reactive, in the present products, the  $\alpha$ -(or the true lactamic) carbonyl group reacts with phenol, resorcin, diethyl-*m*-amidophenol and also pyrogallol, rendering the lactamic ring unstable, and readily opened by alcoholic caustic potash setting free the amido group. In fact, the present compounds may be looked upon as being derived from isatinic acid in the same manner as the amino-benzein (already described), is derived from anthranilic acid,—the two acids being comparable.



Pyrogallol has also been found to condense readily with isatin yielding a product, similar to other pyrogallol derivatives, which gives deeply coloured non-fluorescent solutions in alkalis and organic solvents.

*p*-Cresol has also been condensed with isatin, giving a product insoluble in acids and alkalis, but dissolving readily in glacial acetic acid and conc. sulphuric acid in the latter solvent with slight fluorescence. Its properties are therefore analogous to those of *p*-cresolphthalein anhydride.

#### EXPERIMENTAL.

##### *General observations.*

The following observations may be made regarding the general procedure followed in the preparation of the compounds described in this paper.

One mol. of the acid, ester, lactone, or lactam was heated with two mols. of resorcin, pyrogallol, etc., with powdered anhydrous zinc chloride to 180-200°C, for three to four hours, generally in a current of dry hydrochloric acid. The cases in which this method was departed from is noted under the individual preparations. No

hydrochloric acid gas was used in the preparation of the rhodamines.

The purification of the compounds was effected by powdering the crude product wherever possible, extracting with boiling solution of dilute hydrochloric acid to remove zinc chloride, dissolving the washed residue in dil. caustic soda solution, and precipitating with dil. acetic acid or hydrochloric acid. This operation was repeated two or three times when necessary, and the washed and dried residue crystallized from alcohol, acetone or pyridine as the case might be. In some cases hydrochloric acid precipitated the product in a resinous form from alkaline solutions, in which cases dil. acetic acid was employed instead. In cases where the product was not sufficiently purified by precipitation, it was boiled with animal charcoal in alcoholic solution, and the filtered solution poured into water and then the washed residue crystallized from alcohol, etc.

In some cases, the removal of zinc chloride proved to be a matter of considerable difficulty, and the purification was effected by repeated extraction with hot dil. hydrochloric acid solution, both in the first stage, and in the subsequent stages. In these cases the final purification was effected from acetone.

Bromination was effected by adding slight excess of bromine to an alcoholic solution of the product, and allowing to stand overnight. The ppt. was filtered, washed with hot water, dissolved in caustic soda, precipitated with hydrochloric acid and finally crystallized from alcohol. As mentioned previously, in some cases di-, and in others tetra-bromo derivatives were thus obtained.

The potassium salts were prepared by suspending the finely powdered substance in hot water, adding a slightly less than the theoretical quantity of caustic potash (purified by extraction with absolute alcohol) and

constantly stirring the mixture heated on the water-bath, till solution was complete. It was filtered from the excess of the substance and the filtrate evaporated to dryness on the water-bath. It was then powdered, washed with absolute alcohol, and then extracted with the minimum quantity of water, and the aqueous solution concentrated, when the potassium salt separated.

Only two benzoyl derivatives, those of the salicylic acid and the phenol-phthalein compounds, were prepared by the usual method. As these derivatives contain nearly the same percentage of carbon and hydrogen as the parent substances, and as particularly it was practically impossible in many cases, to distinguish between the mono- or poly-benzoylated products by combustion results, this class of derivatives were not prepared in the case of other compounds.

The rhodamines were generally formed at somewhat lower temps. and less heating was required for their formation. For purification, they were powdered, extracted repeatedly with hot water and hot dil. caustic soda to remove zinc chloride and dissolved in hot dil. hydrochloric acid and precipitated with caustic soda or ammonium hydroxide. This was repeated and the dried product purified from alcohol, acetone or pyridine. In cases of difficulty of purification, the alcoholic solution was boiled with animal charcoal, and the filtered solution was poured into water till a turbidity was produced. The solution was then filtered and allowed to stand overnight with more water. The ppt. which separated was then purified by crystallisation from alcohol, etc.

#### THE CONDENSATIONS WITH ACIDS. (A)

1. *Resorcinol-gallein*.—3.5 gms. of gallic acid and 4.5 gms. of resorcin were heated on the oil-bath till the mixture melted (at about 200°C). At this stage, the flame

was removed, and 3 gms. of zinc chloride were added in small quantities at a time. A vigorous reaction ensued, and the mixture completely melted. The temp. was lowered to  $190^{\circ}\text{C}$  and kept there till the vigour of the reaction subsided. Afterwards the temp. was raised to  $200^{\circ}\text{C}$  and kept there for 3 hours. All this time, a slow current of hydrochloric acid gas was passed over the mixture.

The purification was effected by the general method. Yield 80% of the theoretical. It is a dark-red powder dissolving in alkalis and organic solvents with deep green-red fluorescence. Soluble in alcohol, more so in acetone, insoluble in acetic acid, ether and benzene. Dyes wool and silk brownish shades deepening on chroming. It does not melt up to  $250^{\circ}\text{C}$ . It gives a red di-bromo derivative.

Found:  $\text{C}=67.7, 67.72\%$  ;  $\text{H}=3.96, 4.02\%$  .  $\text{C}_{19}\text{H}_{12}\text{O}_6$  requires  $\text{C}=67.85\%$  ,  $\text{H}=3.6\%$  .

*Di-bromo* derivative—is a red powder, giving red solution in alkali without fluorescence. Dyes wool and silk deep red. It does not melt up to  $250^{\circ}\text{C}$ .

Found:  $\text{Br}=31.97\%$  .  $\text{C}_{19}\text{H}_{10}\text{O}_6\text{Br}_2$  requires  $\text{Br}=32.4\%$  .

2. *Resorcinol-o-amino-benzoin*.—4 gms. of anthranilic acid and 6.8 gms. of resorcin were mixed with 5 gms. of zinc chloride and heated for 4 hours to  $180^{\circ}\text{C}$  in a current of dry hydrochloric acid. Purification was effected as in the case of 'resorcinol salicylein.' (Sen and Sinha, Amer. Chem. J., 1923, 12, 2984.) It was finally crystallized from alcohol and dried in the vacuum desiccator. Yield about 70% of the theoretical. The substance closely resembles resorcinol salicylein in colour, fluorescence, solubilities and dyeing properties. It softens at  $175-77^{\circ}\text{C}$ . It gives a di-bromo, and a mono-potassium derivative.

Found:  $\text{N}=4.36\%$  ,  $4.41\%$  .  $\text{C}_{19}\text{H}_{13}\text{O}_8\text{N}$  requires  $\text{N}=4.6\%$  .

*Di-bromo* derivative.—Closely resembles the bromo-derivative of resorcinol salicylein in properties. Dyes red shades. Decomposes at  $195^{\circ}\text{C}$ . Found:  $\text{Br} = 34.4\%$ .  $\text{C}_{19}\text{H}_{17}\text{O}_3\text{NBr}_2$  requires  $\text{Br} = 34.7\%$ .

*Mono-potassium* derivative.—Dissolves in water with green-red fluorescence changing to bluish-red on standing. Found:  $\text{K} = 11.6\%$ .  $\text{C}_{19}\text{H}_{12}\text{O}_3\text{NK}$  requires  $\text{K} = 11.4\%$ .

3. *Resorcinol-stearcin*.—3 gms. of stearic acid (1 mol.), were mixed with 3.5 gms. (3 mols.), of resorcin and heated with the addition of 3 gms. of zinc chloride to  $200\text{--}210^{\circ}\text{C}$  for  $4\frac{1}{2}$  hours. A large excess of resorcin was employed to prevent the presence of unaltered stearic acid in the final product. To ensure the completion of the reaction the heating was effected for a longer time than usual at a higher temp.

The product was purified by the general method, and finally from benzene. It was dried in the vacuum desiccator. Unlike the other products it was soluble in benzene and to a less extent in ether. The fluorescence was slight but appreciable, and the colour deep red. On standing a bluish tone is assumed. The product has very slight affinity for wool and silk. It softens at  $152^{\circ}\text{C}$ .

Found:  $\text{C} = 79.78, 79.70\%$ .  $\text{H} = 9.5, 9.48\%$ .  $\text{C}_{30}\text{H}_{42}\text{O}_3$  requires  $\text{C} = 80\%$ ,  $\text{H} = 9.33\%$ .

4. *Resorcinol-pyromucein*.—4 gms. of mucic acid and 4 gms. of resorcinol were gradually heated with 4 gms. of zinc chloride in a current of dry hydrochloric acid. At  $140^{\circ}\text{C}$  a vigorous reaction ensued. When it subsided a little, the temp. was gradually raised to  $200^{\circ}\text{C}$  and kept there for  $3\frac{1}{2}$  hours. Purification was effected by the general method. Finally from pyridine. The product is similar to the stearic acid compound in colour and fluorescence, but has more pronounced dyeing properties. It is however insoluble in benzene or ether, and not very soluble in alcohol.



The fluorescence is also slight. It does not melt up to 250°C.

Found: C=73.0%, H=3.9%.  $C_{17}H_{10}O_4$  requires C=73.37%, H=3.6%.

5. *Pyrogallol-salicylein*.—3 gms. of salicylic acid and 5 gms. of pyrogallol were heated with 3.5 gms. of zinc chloride for 4 hours to 180-90°C. Purification was effected by the general method. Finally from a mixture of pyridine and water (2:1). The alkaline solution has a deep red-brown colour, without fluorescence, as also solutions in organic solvents. It is not very soluble in alcohol, but dissolves in acetone, and a mixture of pyridine and water. It does not melt up to 250°C.

Found: C=67.6%, H=3.82%.  $C_{19}H_{12}O_8$  requires C=67.85%, H=3.57%.

6. *Anthranilo-rhodamine*.—3 gms. (slight excess of 1 mol.) of anthranilic acid and 6.5 gms. of di-ethyl-*m*-amido phenol were finely ground together and heated on the oil-bath till the mixture melted. Powdered zinc chloride was added in small quantities with constant stirring. The mixture was then gradually heated to 180°C for 3 hours, till the melt solidified. The cold mass was finely powdered, extracted repeatedly with hot water and hot dil. caustic soda to remove zinc chloride. It was then dissolved in warm dil. hydrochloric acid and precipitated with ammonium hydroxide or caustic soda. This was repeated and the washed residue finally purified from alcohol and obtained in the form of a pink powder. It dissolves readily in acids with green-red fluorescence, more marked in organic solvents. Yield about 60% of the theoretical. It softens at about 230°C. Dyes wool and silk an impure violet shade (with a mixture of green).

Found: N=9.56, 9.62%.  $C_{27}H_{33}O_2N_3$  requires N=9.74%.

## CONDENSATIONS WITH ESTERS. (B)

7. *Resorcinol-salicylein*.—A mixture of 3 gms. of methyl salicylate and 4.5 gms. of resorcin was heated with zinc chloride with an air-condenser in a current of dry hydrochloric acid. The temp. was raised gradually to 200°C and kept there for 4 hours. The purification was effected by the method for the identical product obtained from the acid. Finally purified from acetone. Yield 85% of the theoretical. Does not melt up to 260°C.

Found: C=74.84%, 74.86%; H=4.38, 4.3%.  $C_{10}H_{12}O_4$  requires C=75.0%, H=4.0%.

8. *Pyrogallol-salicylein*.—3 gms. of oil of winter-green and 5 gms. of pyrogallol were heated with 4 gms. of zinc chloride in a current of dry hydrochloric acid for 4 hours with an air-condenser. The product was identical with that obtained from the acid. Yield about 85% of the theoretical.

Found: C=67.64%, H=3.72%.  $C_{10}H_{12}O_6$  requires C=67.85%, H=3.57%.

## CONDENSATIONS WITH LACTONES. (C)

9.  *$\beta$ -Naphthol-coumारेin*.—A mixture of 3 gms. of coumarin and 6 gms. of  $\beta$ -naphthol was heated for 4 hours at 180-90°C in a current of dry hydrochloric acid, together with 4 gms. of zinc chloride. The product was extracted repeatedly with boiling dil. hydrochloric acid solution to remove zinc chloride, washed with hot water, extracted with caustic soda and the solution pptd. with dil. acetic acid solution (hydrochloric acid threw down the substance in a pasty form). The operation was repeated twice. After each precipitation the ppt. was boiled with dil. hydrochloric acid to remove traces of zinc chloride the removal of which was found difficult to accomplish. Purified first from boiling alcohol containing animal charcoal, and then from acetone. (A portion of the

crude product was left after first extraction with caustic soda solution, but was not further investigated.) It was dried in the vacuum desiccator. It is a yellowish brown powder not very soluble in alcohol, but dissolves in acetone, glacial acetic acid and conc. sulphuric acid with green fluorescence. It is pptd. by carbon dioxide from alkaline solution. It softens at  $115^{\circ}\text{C}$ . It has very feeble affinity for animal fibres.

Found:  $\text{C}=83.56, 83.4\%$  ;  $\text{H}=5.2, 4.8\%$  .  $\text{C}_{20}\text{H}_{18}\text{O}_2$ ,  $\text{H}_2\text{O}$ , or  $\text{C}_{20}\text{H}_{20}\text{O}_3$  requires  $\text{C}=83.65\%$  ,  $\text{H}=4.8\%$  .

10.  *$\alpha$ -Naphthol-coumarein.*—3 gms. of coumarin and 6 gms. of  $\alpha$ -naphthol were heated with 4 gms. of zinc chloride in a current of dry hydrochloric acid for 3 hours to  $180^{\circ}\text{C}$ . There was a great deal of tar formation, which reduced the yield to 40% of the theoretical. After preliminary precipitations as in the case of the  $\beta$ -naphthol compound, the product was dissolved in alcohol, and boiled with animal charcoal for 10 minutes. The cooled filtrate was poured into water till a turbidity was produced. It was filtered and the filtrate allowed to stand overnight with more water. The ppt. thus obtained was finally purified from acetone and dried in a vacuum desiccator. It is a dark brown powder dissolving in caustic soda with red colour. It softens at about  $117^{\circ}\text{C}$ . It has no appreciable affinity for animal fibres.

Found:  $\text{C}=80.38, 80.02\%$  ;  $\text{H}=4.89, 4.9\%$  .  $\text{C}_{20}\text{H}_{22}\text{O}_4$  requires  $\text{C}=80.18\%$  ,  $\text{H}=5.07\%$  .

13. *Pyrogallol-coumarein.*—3 gms. of coumarin were heated with 5 gms. of pyrogallol and 3 gms. of zinc chloride to  $180\text{--}90^{\circ}\text{C}$  for 4 hours in a current of dry hydrochloric acid. The product was analogous in properties to other pyrogallol derivatives and purified by analogous method. Finally from alcohol. It does not melt up to  $250^{\circ}\text{C}$ .

Found :  $C=66.2\%$  ,  $H=4.16\%$  .  $C_{21}H_{13}O_6, H_2O$  requires  $C=66.49\%$  ,  $H=3.96\%$  .

14. *Coumarin-rhodamine*.—3 gms. of coumarin and 7 gms. of diethyl-*m*-amido phenol were heated with 3 gms. of zinc chloride to  $180-90^\circ C$  for 3 hours, till the melt completely solidified. The purification was effected as in the case of 'anthranilo-rhodamine.' Only the alcoholic solution was boiled with animal charcoal and to the cool filtrate, water was added till a turbidity was produced. It was filtered, and the filtrate allowed to stand with more water. The ppt. thrown down was filtered, and finally purified from acetone. It dissolves in acids with a violet colour, and greenish fluorescence, more marked in organic solvents. Softens at  $156^\circ C$ . Dyes wool and silk violet shades.

Found:  $N=6.16, 6.2\%$  .  $C_{29}H_{32}O_2N_2$  requires  $N=6.36\%$  .

15. *Phenol-resorcinol-phthalein*.—6.5 gms. (1 mol.) of phenol-phthalein, and 5.5 gms. ( $2\frac{1}{2}$  mols.) of resorcin, were heated with 5 gms. of zinc chloride to  $110-15^\circ C$  for  $4\frac{1}{2}$  hours. Purified by the general method. Finally from alcohol. Yield 70% of the theoretical. It is an orange powder somewhat soluble in hot water, more so in acetone, alcohol. The alkaline solution shows a fluorescence of the same nature and degree as fluorescein. It does not melt up to  $250^\circ C$ . It gives a tetra-bromo, and a di-potassium, and a di-benzoyl derivative. Dyes a greenish yellow shade.

Found:  $C=76.23, 76.30\%$  ,  $H=4.38, 4.52\%$  ,  $C_{32}H_{22}O_6$  requires  $C=76.47\%$  ,  $H=4.4\%$  .

*Tetra-bromo* derivative.—Orange powder dissolving in alkalis with some fluorescence. Dyes wool and silk red shades. It does not melt up to  $250^\circ C$ . Found:  $Br=39.3\%$  .  $C_{32}H_{18}O_6Br_4$  requires  $Br=39.1\%$  .

*Di-potassium* derivative.—Found:  $K=13.9\%$  .  $C_{32}H_{18}O_6K_2$  requires  $K=13.8\%$  .

*Di-benzoyl* derivative.—Melts at 156-58°C. Found: C=77.5%, H=4.4%.  $C_{40}H_{30}O_8$  requires C=77.74%, H=4.22%.

15A. *Fluorescein*.—3.2 gms. of phenol-phthalein were heated with 2.5 gms. of resorcin, with 2.5 gms. of zinc chloride for 3 to 4 hours to 180-200°C. The purification was effected by the general method. Finally crystallized from alcohol. It has all the properties of fluorescein.

Found: C=72.36%, H=4.0%. Fluorescein,  $C_{20}H_{12}O_6$  requires C=72.3%, H=3.7%.

16. *Resorcinol-p-cresolphthalein*.—3.3 gms. of *p*-cresolphthalein anhydride and 2.5 gms. of resorcin were heated together with zinc chloride to 200-220°C for 4½ hours in a current of dry hydrochloric acid. It was purified by the general method, finally from acetone. It is a red powder, soluble in caustic soda with green-red fluorescence less bright than that of fluorescein. It is precipitated by carbon dioxide from this solution. Soluble in acetone and pyridine, less soluble in alcohol. Softens at about 220°C. Gives a di-potassium derivative.

Found: C=79.36, 79.42%; H=5.0, 4.92%.  $C_{34}H_{24}O_5$  requires C=79.68%, H=4.67%.

*Di-potassium* derivative.—Found: K=12.9%.  $C_{34}H_{22}O_5K_2$  requires K=13.2%.

17. *Resorcinol-fluorescein*.—3.5 gms. (1 mol.) of fluorescein, and 3.5 gms. (3 mols.) of resorcin, were heated together with 4 gms. of zinc chloride for 5 hours to 230-40°C. The purification was effected, after removal of zinc chloride by extracting the product with sodium carbonate solution to remove unchanged fluorescein. It was then washed, dissolved in caustic soda and pptd. with carbon dioxide. It was re-dissolved in caustic soda pptd. by hydrochloric acid, dried, and purified finally from a mixture of pyridine and water (2:1). The product unlike

fluorescein is insoluble in sodium carbonate. Alkaline solutions have a fluorescence less bright than that of fluorescein. It decomposes at about 230°C.

Found: C=73.86, 73.93%; H=3.84, 3.86%.  $C_{32}H_{20}O_7$  requires C=74.4%, H=3.87%. Fluorescein requires C=72.2%, H=3.7%.

#### CONDENSATIONS WITH LACTAMS. (D)

18. *Resorcinol-isatinein*.—3 gms. of isatin and 4.5 gms. of resorcin were heated for 3 hours with zinc chloride to 180-90°C, in current of dry hydrochloric acid. The purification was effected by the general method. Finally from alcohol. Yield about 75% of the theoretical. It is an orange powder, dissolving in alkalis with slight fluorescence, more marked in conc. sulphuric acid solution. Does not melt up to 265°C. It dyes wool and silk orange shades from an acid bath. It gives a di-potassium and a tetrabromo derivative.

Found: N=3.84, 3.98%.  $C_{30}H_{15}O_4N$  requires N=4.2%.

*Di-potassium* derivative.—Found: K=19.5%.  $C_{30}H_{11}O_4K_2N$  requires K=19.2%.

*Tetra-bromo* derivative.—Dyes red shades. Decomposes at 230°C. Found: Br=49.7%.  $C_{20}H_9O_4NBr_4$  requires Br=49.4%.

19. *Isatin-rhodamine*.—3 gms. of isatin and 6.5 gms. of diethyl-*m*-amido phenol were heated with 4.5 gms. of zinc chloride for 3 hours to 180°C. The purification was effected as in the case of the anthranilic acid compound. Finally from acetone. Dissolves in acids with a green-red fluorescence. It softens at 242°C. It dyes wool and silk an impure violet shade.

Found: N=9.3, 9.2%.  $C_{28}H_{31}O_2N_3$  requires N=9.5%.

20. *Pyrogallol-isatinein*.—3.5 gms. of isatin and 6 gms. of pyrogallol were heated with 4 gms. of zinc chloride

for 3 hours to 180°C. Purification was effected by the general method. Finally from acetone. It has properties similar to other pyrogallol derivatives, giving non-fluorescent deeply coloured solutions in alkalies and organic solvents. Does not melt up to 250°C.

Found :  $N=3.7$ ,  $3.74\%$ .  $C_{20}H_{13}O_6N$  requires  $N=3.86\%$ .

21. *Phenol-isatinein*.—3.5 gms. of isatin and 3 gms. of phenol were heated with 4 gms. of zinc chloride for 4 hours to 190°C. The product was steam-distilled and the residue purified by the usual method. Finally from alcohol. The product is a greyish powder dissolving in alkalies with a red colour. It softens at about 285°C.

Found :  $N=4.2$ ,  $4.24\%$ .  $C_{20}H_{15}O_5N$  requires  $N=4.41\%$ .

22. *p-Cresol-isatinein anhydride*.—3.5 gms. of isatin and 5.5 gms. of *p*-cresol were heated together with 4 gms. of zinc chloride in a current of dry hydrochloric acid for  $2\frac{1}{2}$  hours at 180°C. The product after removal of zinc chloride was extracted with glacial acetic acid and the solution poured into water. The ppt. was filtered, washed and crystallized from glacial acetic acid. Obtained as a greyish powder. Dissolves readily in acetic acid and in conc. sulphuric acid with faint fluorescence. Does not melt up to 250°C.

Found :  $N=4.0\%$ .  $C_{22}H_{17}O_2N$  requires  $N=4.28\%$ .

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# **Electro-osmotic Experiments on Intensity of Adsorption of a Constituent Ion by an Insoluble Salt.**

## **Part I.**

BY

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AND

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A heteropolar precipitate like that of an insoluble salt has a tendency to adsorb its constituent ions from aqueous solutions. It seems that this type of adsorption is responsible for several phenomena which do not at first sight appear to be correlated. Lottermoser observed that precipitated silver salts pass into the colloidal state when the solution contains one of the common ions in excess. The charge of the colloid is of the same sign as that of the constituent ion which is present in excess in the solution. Marc from his experiments on the adsorption by crystalline surfaces [Z. phys. Chem., 75, 710 (1911); 81, 641 (1913)] concluded that a crystalline substance adsorbs only those dissolved substances which can form isomorphous compounds with the crystal or compounds which have similar crystalline forms. Fajans and Beer [Ber., 46, 3486 (1913); also 48, 700 (1915)] pointed out that the separation of a radio-element from its solution by an insoluble salt takes place only when the radio-element itself can form an insoluble precipitate. Paneth and Horowitz [(Z. Phys. Chem. 89, 513, (1915); also



Phys. Z. 15, 924 (1914)] recognised in view of Marc's work that the separation of radio-elements, by precipitates is due to the adsorption of the radio-element, and that a radio-element will be adsorbed by an insoluble heteropolar adsorbent only when it can form an insoluble salt. Paneth however, considers that the adsorption of the radio-element consists in an actual exchange of places between ions in the crystal lattice and the radio-elements in solution. Thus barium ions in barium sulphate are replaced by radium ions from solution and the barium ions pass into solution.

It has been pointed out by the writer that in the case of a large number of colloidal suspensoids, the stabilising electrolyte has an ion in common with the colloid, and that the adsorption of a common ion by a precipitate is a simple consequence of the modern view of the structure of crystals of salts. (Far. Soc. Disc. October, 1920; published October, 1921.) The adsorption of an ion imparts a charge to the surface and thus tends to peptise the precipitate. It has been further pointed out (Mukherjee, *loc. cit.*; Phil. Mag., 1922, VI, 44, p. 327) that there is an essential difference in the manner of adsorption as pictured by Paneth and that which must be assumed to account for the stability of colloids. The type of adsorption suggested by Paneth will not impart a charge to the surface and hence cannot account either for the observations on the charge of colloids in the presence of peptising electrolytes or for their stability. The exchange of ions between the crystal lattice and the solution must be a slow process, when the salt is only sparingly soluble, whereas the adsorption of ions by the surface will be much quicker. Both types of adsorption have probably to be taken into account, but it appears

from the literature on colloids that the adsorption of ions as such by the surface is more frequent than an actual interchange of ions as conceived by Paneth. Experimental evidence will be adduced in the sequel in support of this view.

Another class of phenomena is also probably closely connected with the adsorption of constituent ions by a precipitate. Bradford [(*Biochem. J.* ; 10, p. 169 (1916), 11, p. 14 (1917)] has suggested that the adsorption of the precipitating ions is at least partly responsible for the formation of Liesegang rings. The adsorption of constituent ions may also affect the permeability of the precipitate to the diffusing ions—a factor which also probably plays an important role in the formation of Liesegang rings. (Fischer, *Koll. Zeit.* 30, 1920, p. 13.)

The experiments of Debye and Scherrer have shown that colloidal particles have the same crystalline structure as they have in large masses or well-developed crystals. One has, of course, to remember that the surface forces acting on constituent ions existing in the solution are not exactly similar to those acting on the ion in the interior of the lattice. (Madelung, *Phys. Z.* 20, 494, 1919). But such considerations do not materially affect the validity of our point of view.

Fajans and Beckerath (*Z. Phys. Chem.* 97, 1921, 4/8) have suggested an explanation similar to ours regarding the adsorption of a constituent ion by a crystal lattice. They have further attempted to consider the energy required to separate an adsorbed ion from the surface in the light of the work necessary to separate the constituent ions from the crystal lattice and the energy change due to hydration. These authors consider that there is a close relationship between the

intensity of adsorption of the ions by the surface and the solubility of the corresponding salt (*loc. cit.*, p. 500). Langmuir (J. Amer. Chem. Soc. 38 (1916) 2221; 39, 1917, 1848), considers the intensity of adsorption to be determined by the energy changes associated with the process. So far no very definite result has been obtained from this treatment as the energy changes associated with the process of adsorption do not admit of easy theoretical calculation and the estimates of the energy change are based on more or less arbitrary assumptions. It would appear from the sequel that Fajans's method of treatment is too simple to account for the intensity of adsorption of ions.

The present investigation deals with the adsorption of ions by precipitated and carefully washed lead chromate. This substance was selected because it has been used in many cases for the investigation of Liesegang rings. Moreover there is a large number of insoluble lead salts and it is of interest to compare the relative intensity of adsorption of different anions by a surface of lead chromate with the solubility products of the corresponding salt.

The amounts of ions adsorbed has been mostly measured from chemical analysis, or from measurements of activity where the sensitive radio-active methods can be used. These methods do not give any indication as to whether the adsorbed ions replace those of the same sign in the crystal lattice thus leaving the crystal and its surface electrically neutral or are adsorbed on the surface with or without exchange of ions and the surface becomes electrically charged, through an excess in the adsorption of ions of one sign. Electro-osmotic measurements can decide between these two possibilities. Moreover, it is more convenient and accurate than analytical methods. It may be noted here that recently several investigators

have emphasised the necessity of considering simultaneous adsorption of the solvent and of the solute. The analytical result represents the net effect. One cannot therefore simply say that so much of the solute has been adsorbed. In fact some assumptions about the relative adsorptions of the solute and the solvent have to be made in order that an actual idea of the adsorption of the solute can be made (*cf.* Wo. Ostwald and Izagguire, *Koll. Z.* 30, 1919, 279, also previous literature). Of course it is possible that for the dilute solutions with which we are dealing, the adsorption of the solvent can be assumed to be more or less constant. But if there be alterations in hydration, on the adsorption of ions consequent on the variation in the electric charge, then we have a fresh source of disturbance and analytical data do not give a clear idea of the adsorption.

#### EXPERIMENTAL.

The arrangement used for the electro-osmotic measurements is a modified form of that used by Briggs the straight tube being replaced by a U-tube which does away with the use of porous plugs or glasswool (*cf.* Mukherjee, *Nature*, Dec. 2, 1922). The method gives results accurate within  $\pm 7\%$ . The position of the electrodes in the U-tube did not vary during these experiments. The same U-tube and the glass tube connections were used throughout these experiments. The U-tube was always filled with the precipitated lead chromate between two marks symmetrically placed one on each limb of the U-tube. The precipitate was stirred with water or electrolyte and then poured in the U-tube and allowed to settle for 24 hours. The excess of lead chromate was drawn off with a pipette. The thickness of the layer of the precipitate was 12.8 cm. The preparation

and purification of the precipitate requires great care. Chemically pure lead nitrate was further purified by recrystallisations. The crystals were powdered and dried at  $102^{\circ}$ . Chemically pure potassium chromate was carefully washed in a Buchner funnel. Two solutions of lead nitrate and potassium chromate of equal strength were prepared and lead-chromate was precipitated by addition of equivalent amounts of the two solutions from a burette into a beaker with silver nitrate as outside indicator.

The supernatant liquid was poured out and the precipitate was digested in pure boiling water for half an hour and the supernatant liquid was again poured out. The finer particles were removed along with the supernatant liquid. The process was repeated 10-12 times. It appears that potassium chromate was adsorbed in perceptible quantities during the precipitation, though the supernatant liquid after precipitation showed no trace of chromate with silver nitrate. During the first two digestions, the supernatant liquid assumed a yellow colour after some time, but in subsequent washings remained quite colourless. The substance becomes more free from adsorbed chemicals with repeated digestions. The digested and wet lead chromate was kept in stoppered resistance glass bottles in a place free from fumes.

Differences in the size of the air bubble within fair limits do not influence its velocity for the same experimental arrangement.

Every experiment was carried out under exactly similar conditions. The electric current is switched on for five minutes and the tube is then allowed to rest till the air-bubble becomes stationary, and the distance the bubble has moved is noted. The direction of the current is then reversed, and the mean of the two readings is taken. This was repeated at least five times in each case and their

mean was taken. The different readings do not differ by more than  $\pm 5\%$ .

When electrolytes were used, the same amount of the precipitate was washed with the electrolyte solution several times to ensure that the concentration of electrolyte taken remains unchanged after removal of the water and after adsorption. The results are given below. The method is not free from certain sources of error and it is intended to investigate them with a view to modify the experimental arrangements. It may be added that the usual method is sufficiently accurate for our present purpose.

At high electrolyte concentrations the acids set free on electrolysis of the salt solution convert the chromate into dichromate with the consequent change in colour.

The velocity of the bubble is proportional to the density of the electrical charge on the surface. Since

$$v^* = \frac{c \cdot H \cdot q \cdot \delta}{\eta}$$

where  $v$  = velocity in cms/sec (of the bubble).

$H$  = pot. grad ant.

$q$  = sectional area.

$c$  = density of electrical charge;  $\delta$  = the thickness of the double layer and  $\eta$  = co-efficient of viscosity.

$H$  and  $q$  are constant under the conditions of the experiment.  $\eta$  may be taken to be constant for these dilute salt solutions, and  $\delta$  is assumed to be constant.

\* We have taken the usual form of the equation cf. (Freundlich, *Kapillarchemie*, 1922, p. 328).

TABLE I.

*Lead Chromate.*Velocity in cm. per sec.  $\times$  300.

Electrolytic conc.	Water.	KCl.	K <sub>2</sub> CrO <sub>4</sub> .	Pb(NO <sub>3</sub> ) <sub>2</sub> .	KNO <sub>3</sub> .	K <sub>2</sub> SO <sub>4</sub> .	BaCl <sub>2</sub> .	KI.	KIO <sub>3</sub> .	CaCl <sub>2</sub> .
O	18.2	..	..	..	..	..	..	..	..	..
N/15000	..	22.0	..	..	..	..	..	..	..	..
N/5000	..	23.0	25.1	7.1	20.2	22.6	20.2	22.7	26.6	21.4
N/4000	..	26.6	..	..	..	..	..	..	..	..
N/2500	..	28.1	..	..	..	..	..	..	..	..
N/2000	..	29.8	35.3	-3	31.3	32	20.7	30.5	32.5	25.5
N/1000	..	32.4	44.9	-7.9	32.8	38.5	17.5	Decomposition sets in	36.3	25.5
N/500	..	36.8	..	..	..	..	14.3	..	..	..
N/250	..	Decomposition sets in			..	..	..	..	..	..

## DISCUSSION.

The readings with water alone show that the substance is negatively charged in contact with water. We are not sure whether the negative charge owes its origin to the adsorption of chromate ions which probably could not be removed even after 13 digestions with pure boiling water, or to the adsorption of hydroxyl ions from water.\* It will be seen from the above that of the four cations, K, Ba, Pb and Ca, only Pb<sup>++</sup> ions materially affect the velocity of the bubble, diminishing it markedly at as low a concentration as n/5000 and at a higher concentration n/1000, the bubble moves in the opposite direction.

\* The question will be dealt with in a second communication.

These experiments bring out undoubtedly that the adsorption of the positively charged lead ion at first decreases the density of the negative charge on the surface till at a higher concentration, the surface positively becomes charged being covered with an excess of lead ions. It would have been of great interest to follow the the increase in charges still further with increasing concentration, but the transformation of chromate unfortunately prevents further observation.

The marked adsorption of the lead ions in contrast to that of the other cations can be readily understood if we remember that it is a constituent ion of the precipitate (*cf.* Mukherjee, *Far. Soc. Disc. Oct. 1922* ; *Phil. Mag.*, *loc. cit.*).

A comparison of the effects of K, Ba or Ca will show that for the same anion,  $Ba^{++}$  ions are more adsorbed than  $Ca^{++}$  ions and that  $K^{+}$  ions are least adsorbed.

On the other hand, of the anions the chromate which is the other constituent ion has a great effect on the charge. In general, on the addition of an electrolyte other than the lead salt, there is an increase in the negative charge to begin with. In the case of  $BaCl_2$  the charge at first remains constant up to a concentration of  $N/2000$  and then begins to decrease. This is a very common feature of the curves between the charge and the concentration of the electrolyte, when the oppositely charged ion is weakly adsorbed (*cf.* Mukherjee, *Phil. Mag.* VI, 44, 1922, pp. 328 *et. seq.*). In the case of  $CaCl_2$  the anion effect predominates within the limits of concentration studied, the density of the charge being always greater than that with pure water. The cation effect is however apparent if we compare the relative



effects of calcium chloride, potassium nitrate and potassium chloride.

A quantitative comparison of the relative intensities of adsorption of individual ions is not easy. The observations show that adsorption of both ions at these low concentrations has to be considered. For the different potassium salts it is permissible to compare the relative anion effects, as the cation is the same in each case. In comparing the intensities of the adsorption of the anions, the valency of the anion has to be taken into account. For the same increase in the density of the negative charge, the *amount* of an anion adsorbed is inversely proportional to its valency. Since we know the valency and the increase in the densities of the charge compared to that for pure water, we can compare the relative amounts of the different anions adsorbed. Such a comparison is however not free from objections. First of all, the assumption (*loc. cit.*) of a constant thickness of the double layer is not certainly self-evident. Secondly, we do not know exactly the source of the charge of the surface in contact with water and a replacement of the ions already existing on the surface by the ions of the same charge present in the solution, will not alter the charge and will escape detection. Consequently, even if adsorption takes place there may be no alteration in the charge. The error due to this cause will however be smaller, when the change in charge is great. For this reason, we have taken the values at  $\cdot 0005N$  for comparison. Probably the initial charge is due to the adsorption of chromate ions as it is almost impossible to remove the last traces of adsorbed electrolytes by washing or by digestion with boiling water in many cases. The only other source may be the adsorption of hydroxyl

ions from water. Lastly the variation in the charge is due to the adsorption of two ions of opposite sign and it is evidently erroneous to refer all of the observed difference to the adsorption of one ion only. These objections are not likely to influence the general nature of the conclusions we have drawn from the comparison outlined above. Since we have at present no idea as to what determines the thickness of the double layer, we might leave it out of account, though it is probable that the thickness of the double layer depends on the density of the electrical charge. This is justifiable to some extent on the ground, that so far conclusions drawn from the assumption, that the velocity of electro-osmosis, or cataphoresis is proportional to the density of the electrical charge on the surface, have helped us consistently to explain colloidal phenomena associated with electrical charge of particles. Regarding the last objection we might neglect the adsorption of the weakly adsorbed ion, in comparison to that of the other as a first approximation, as the great change in the charge shows the preponderating effect of the one over that of the other. In order to form an idea of the relative intensity of adsorption, we must compare the amounts of the anions adsorbed at the same gm. anion concentration. The difference in the velocity is proportional to the net amount of positive or negative charge adsorbed in the form of ions (of both sign) per unit surface. If we compare the potassium salts, we may assume the adsorption of the cation to be constant and the increase in the velocity (*i. e.* of the negative charge) is then proportional to the number of ions adsorbed, multiplied by its valency. The amount of the different anions adsorbed is then given by the increase in velocity (referred to the value for water) divided by the valency of the anion. The following table shows

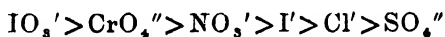
the values for a concentration of  $\cdot 0005$  gm. anion per litre.

TABLE II.

*Potassium Salts.*

Anions.	Conc. in gm. ions per litre.	Difference in velocity	Valency	Amount adsorbed
Cl'	$\cdot 0005$	29·8-18·2	1	11·6
NO',	$\cdot 0005$	31·3-18·2	1	13·1
SO'',	$\cdot 0005$	38·5-18·2	2	$\frac{20\cdot3}{2} = 10\cdot15$
CrO'',	$\cdot 0005$	44·9-18·2	2	$\frac{2\cdot\cdot7}{2} = 13\cdot35$
I'	$\cdot 0005$	30·5-18·2	1	12·3
IO',	$\cdot 0005$	32·5-18·2	1	14·3

The anions arrange themselves in the following order:—

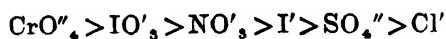


The order given above does not exactly represent the *relative* intensities of adsorption for anions of different valency. The adsorption of chromate and sulphate ions must be greater than that indicated above for two reasons.

(1) Now the velocity of osmosis indicates the net negative charge being the actual charge due to the adsorbed anions less the charge due to the fixed layer of cations. Since we are comparing equal gram-anion concentrations, the concentration of cation will be double for the divalent anions of what it is for univalent anions. The adsorption of the cations is not negligible and the amount of cation adsorbed at the higher concentration will be greater. So that the same velocity

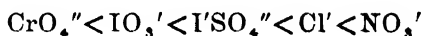
of movement of the bubble at equal gram-anion concentration would indicate a higher adsorption of divalent anions than of univalent anions, or in other words more chromate and sulphate ions are actually adsorbed than are represented by the figures 13·35 and 10·15.

(2) Secondly the density of the negative charge (44·9) for chromate ion is much greater than that in the case of iodate ions (32·5) and the greater negative charge diminishes to a greater extent the number of collision of the anions on the charge. The adsorption of an ion depends on the intensity of adsorption, *i.e.*, on the energy change associated with the process of adsorption by a neutral surface and on the number of collisions on the surface. In the case where we are dealing with the adsorption of ions, carrying an electrical charge of the same sign as that of the adsorbing surface, the number of collisions evidently do not depend on the concentration of the anion. Only those ions can strike on the surface which have sufficient kinetic energy to overcome the electrical repulsion when it approaches the surface. The greater, the negative charge of the surface, the fewer the collisions of the anion on the surface as compared to the probable number of collisions if the surface were neutral. The greater negative charge of the solid in contact with potassium chromate makes the further adsorption of chromate ions more difficult than in the case of the iodate ions of the same gram-anion concentration. If the electrical conditions were identical, the adsorption of the chromate ions would have been greater than that indicated above. We may therefore take the order to be



which is also the order of the increasing solubilities of the

lead salts expressed in terms of gr. atomic concentration of lead,



with the exception of the nitrate.

A strict comparison between the order of adsorbability and of solubility is therefore not possible. Further solubility of the corresponding salt is not a measure of the change in energy when an ion passes from the adsorbed layer in the surface to the solution. For the same reason, a comparison of the lattice energy and of the intensity of adsorption is also not possible without further assumptions regarding the energy of hydration and regarding the effect of adsorption on the hydration of the ion and on the hydration of the surface (Fajans, *loc. cit.*). We, therefore think that Fajans's conclusions as to the relationship between solubility and intensity of adsorption are untenable. It is however remarkable that the order for the other anions is practically the same as that suggested by Fajans.

#### SUMMARY AND CONCLUSIONS.

It is possible to draw certain definite conclusions from the experiments recorded here.

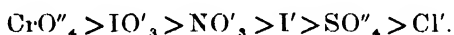
(1) A well-digested precipitate of lead chromate is not electrically neutral against water. The negative charge is probably due to the adsorption of chromate ions or in the alternative hydroxyl ions from water or of both. If the latter view were true, we may observe "hydrolytic adsorption" if the hydrogen ions in the second layer can be replaced by a cation from a neutral solution of a salt *e.g.*, sodium chloride we will have an acid extract.

(2) The order of adsorbability of the cations is



The adsorbability of lead ions is the strongest amongst the cations. It is also very probable that besides the lattice energy of the ions, there are other factors such as the energy of hydration of the surface or of the ion which determine the intensity of adsorption, *i.e.*, the work necessary to separate an ion from the surface to the interior of the solution.

(3) The order of adsorption of anions is probably



The adsorption of chromate is probably the strongest.

(4) The constituent ions of a precipitate are very strongly adsorbed by it. Lead ions being so largely adsorbed as to reverse the charge. This observation suggests the possibility of preparing electrically neutral precipitates. As pointed out above, experiments with electrically neutral lead chromate will enable us to have a better idea of the intensity of adsorption of the different ions. The great intensity of adsorption of the constituent ions is in agreement with the views set forth in a previous paper.

(5) It is of great interest to note that the adsorption of the constituent ions does not consist simply in the exchange of an ion in the crystal lattice with an ion in the solution, as assumed by Paneth. Ions are actually fixed on the surface imparting a charge to it and the type of adsorption considered by Paneth cannot explain the observations recorded here.

(6) Fajans's suggestion that there is a parallelism between the intensity of adsorption of an ion and the solubility of the salt of the adsorbed ion and the ion

with opposite sign in the precipitate is not tenable as the nitrate ion is adsorbed more strongly than the iodide or sulphate.

The method of treatment developed here is capable of other interesting applications.

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*Recd. Aug. 2, 1924*

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# The Oxidation of Triethylene Tetrasulphide by means of Potassium Permanganate.

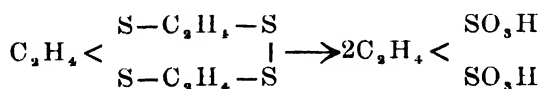
BY

SIR PRAFULLA CHANDRA RÂY.

## Part I.

### Oxidation with Alkaline Potassium Permanganate.

The oxidation of triethylene tetrasulphide with nitric acid has been shown to result in the break-up of the molecule with the formation of the corresponding disulphonic acid. Each of the sulphur atoms situated between a pair of carbon atoms is converted into a sulphone group while fission takes place between the two contiguous sulphur atoms with the formation of the sulphonic acid (J. C. S. Trans., 1923, 123, 2176). It seemed desirable to study the action of a less drastic oxidising agent like potassium permanganate which might be expected to yield the corresponding tetrasulphone. This expectation has been realised as will be shown below under Part II. When, however, the tetrasulphide is treated with alkaline potassium permanganate, instead of a tetrasulphone being formed, it breaks up according to the following scheme :



### EXPERIMENTAL.

The tetrasulphide was suspended in water and treated with about 10 c. c. of a 3% solution of potassium permanganate and a little caustic potash solution. The



addition of the permanganate was repeated till there was a distinct excess of it. The temperature was all along kept at about  $30^{\circ}$ . The reaction was completed by finally heating on the water-bath. The mixture was cooled and the precipitated manganese peroxide brought into solution by passing sulphur dioxide. The solution was concentrated and the potassium and manganese sulphates which crystallised out were filtered off. Alcohol was next added to the concentrated liquid and the precipitate rejected. The alcohol was driven off, the residue dissolved in water and treated with barium carbonate. The precipitate was filtered off and the solution on evaporation gave crystals of the barium salt of ethylene disulphonic acid. The salt was air-dried and was found to be semi-hydrated. (Found: Ba=40.97; S=20.75.\*  $C_2H_4S_2O_6Ba, \frac{1}{2}H_2O$  requires Ba=41.02; S=19.16 per cent.).

## Part I.

### Oxidation with acid Potassium Permanganate.

On oxidation of the triethylene tetrasulphide with potassium permanganate in dilute sulphuric acid solution, a very interesting result is obtained. The expected sulphone formed during the reaction combines with the manganous sulphate produced and a stable double compound of the formula  $[(C_2H_4)_3S_4O_6], MnSO_4, 6H_2O$  is invariably obtained. It has been found to be very sparingly soluble in the cold but dissolves readily in boiling water from which it crystallises out in the pure state. By adding

\* The sulphonate was converted into sulphate by fusion with a mixture of  $KNO_3$  and  $Na_2CO_3$ . The 'melt' was repeatedly evaporated with conc.  $HCl$  to convert the excess of the nitrate as far as possible into the chloride. When the solution is treated with  $BaCl_2$  a portion of the unconverted nitrate is almost invariably carried down with the  $BaSO_4$ ; hence the p. c. of sulphur generally comes out a little too high.

barium chloride to this boiling solution, the corresponding compound with barium sulphate is at once thrown down. By a similar treatment compounds with the sulphates of calcium and strontium as also of potassium and lead have been obtained. With silver nitrate a double compound of silver sulphate is formed. Corresponding double compounds with the sulphates of nickel, cobalt, and copper have also been obtained by the addition of the respective chlorides. Peculiar interest attaches to some of these compounds, notably the combination of the sulphone with barium sulphate, as on account of its extreme insolubility all attempts to combine it with other compounds have hitherto been unsuccessful. But by following this indirect method, however, an additive compound with barium sulphate has been obtained. The sodium compound could not be isolated in a pure condition by a method analogous to that for the preparation of the potassium compound, a special procedure was therefore adopted.

In all these compounds the proportion of the respective metallic sulphate to the sulphone holds simple integral relationship. In the case of the barium compound alone the components are in the simple ratio of 1 : 1 ; whereas they are in the ratio of 2 : 3 in the manganese, copper, cobalt and nickel compounds. The ratio is as 4 : 5 in the potassium, calcium, strontium, silver and lead double compounds. The sodium compound alone gives a ratio of 4 : 1 between sodium sulphate and the sulphone.

#### EXPERIMENTAL.

*The Oxidation of Triethylene Tetrasulphide with Acid Potassium Permanganate.*—The tetrasulphide was treated with a mixture of a concentrated solution of potassium

permanganate and dilute sulphuric acid in small quantities at a time and heated on the water-bath. This process was continued till there remained a distinct excess of the permanganate. The oxidation was complete in the course of about 4 to 6 hours. The excess of permanganate was removed by passing a current of sulphur dioxide through the mixture. The solution became hot, leaving a residue of the unacted tetrasulphide, the latter was filtered off and the filtrate concentrated on the water-bath to nearly half its volume. On cooling, a colourless compound crystallised out. This was filtered, washed with cold water, and dried. (Found: Mn=7.38; S=28.88.  $1\frac{1}{2}[(C_2H_4)_3S_4O_8]$ ,  $MnSO_4$ ,  $6H_2O$  requires Mn=7.15; S=29.13 per cent.).

*Calcium Compound.*—The manganese compound was dissolved in boiling water and a concentrated solution of calcium chloride added to it. A white crystalline calcium compound was at once precipitated, which was filtered and dried. (Found: Ca=7.09; C=16.81.  $1\frac{1}{4}[(C_2H_4)_3S_4O_8]$ ,  $CaSO_4$  requires Ca=7.13; C=16.04 per cent.).

*Strontium Compound.*—This compound was prepared by a process similar to that used for the preparation of the calcium compound. (Found: Sr=14.68; C=14.66.  $1\frac{1}{4}[(C_2H_4)_3S_4O_8]$ ,  $SrSO_4$  requires Sr=14.38; C=14.80 per cent.).

*Barium Compound.*—This compound was also prepared like the calcium compound. (Found: Ba=23.24; S=26.25.  $[(C_2H_4)_3S_4O_8]$ ,  $BaSO_4$ ,  $H_2O$  requires Ba=23.18; S=27.07 per cent.).

*Lead Compound.*—Lead chloride was dissolved in hot water and added to a solution of the manganese compound in boiling water. The precipitate was filtered, washed with hot water and dried. (Found: Pb=28.35.  $1\frac{1}{4}[(C_2H_4)_3S_4O_8]$ ,  $PbSO_4$  requires Pb=28.44 per cent.).

*Silver Compound.*—On adding a very concentrated solution of silver nitrate to a boiling solution of the manganese compound a white precipitate was at once thrown down. (Found:  $\text{Ag}=29\cdot68$ .  $1\frac{1}{4}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$ ,  $\text{Ag}_2\text{SO}_4$  requires  $\text{Ag}=29\cdot31$  per cent.).

*Copper, Cobalt and Nickel Compounds.*—These products were obtained by adding a concentrated solution of the respective chlorides to a concentrated solution of the manganese double compound in hot water. The mixture on concentration and cooling gave crystals which were filtered, washed with a little cold water and dried. These compounds are fairly soluble in hot water. The copper compound is slightly bluish in colour. (Found:  $\text{Cu}=9\cdot06$ ;  $\text{S}=29\cdot55$ .  $1\frac{1}{2}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$ ,  $\text{CuSO}_4$ ,  $4\text{H}_2\text{O}$  requires  $\text{Cu}=8\cdot50$ ;  $\text{S}=30\cdot23$  per cent.). The nickel compound is slightly greenish in colour. (Found:  $\text{Ni}=8\cdot55$ ;  $\text{S}=30\cdot03$ .  $1\frac{1}{2}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$ ,  $\text{NiSO}_4$ ,  $4\text{H}_2\text{O}$  requires  $\text{Ni}=7\cdot97$ ;  $\text{S}=30\cdot40$  per cent.). The cobalt compound has a slight pink tint. (Found:  $\text{Co}=8\cdot23$ ;  $\text{S}=29\cdot28$ .  $1\frac{1}{2}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$ ,  $\text{CoSO}_4$ ,  $4\text{H}_2\text{O}$  requires  $\text{Co}=8\cdot00$ ;  $\text{S}=30\cdot39$  per cent.).

The retention of the characteristic colours of the different metallic double compounds proves that the copper, nickel or cobalt atom does not form a component part of a complex.

*Potassium Compound.*—This compound was obtained as before by adding a concentrated solution of potassium chloride. There was no precipitate while the solution was hot, but on cooling a crystalline compound separated out. (Found:  $\text{K}=12\cdot79$ .  $1\frac{1}{4}[(\text{C}_2\text{H}_4)_3\text{S}_4\text{O}_8]$ ,  $\text{K}_2\text{SO}_4$  requires  $\text{K}=13\cdot02$  per cent.).

*The Sodium Compound.*—An aqueous solution of sodium carbonate was gradually added to a solution of the manganese compound till manganous carbonate was completely precipitated. This was filtered off and the

filtrate concentrated to a small bulk. On adding alcohol to this concentrated solution a syrup was obtained, which crystallised on keeping in a vacuum desiccator. The crystals were dissolved in water and reprecipitated with alcohol. (Found: Na=18·26; S=25·87.  $\frac{1}{4}[(C_2H_4)_3S_4O_8]$ ,  $Na_2SO_4$ ,  $H_2O$  requires Na=18·77; S=26·12 per cent.).

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# On Coagulation of Hydrosols by mixture of Electrolytes and Ionic Antagonism.

BY

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AND

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In a recent paper Freundlich and Scholz (*Kolloid. Chem. Beihefte*, 16, 267, 1922) have shown that the precipitating concentration of barium chloride is materially increased if the electrolyte contains in addition lithium chloride in concentrations which are not in themselves sufficient to cause coagulation. This effect has been observed with hydrosols of arseniousulphide and of sulphur prepared by Oden's method whereas for hydrosols of gold and of sulphur prepared by Weimarn's method the precipitating concentrations remain practically unaffected by such additions. It seems, as it were, the coagulating power of these cations decrease in the presence of a second cation. They found that this antagonism is very pronounced between univalent and divalent cations.

The greatest antagonism was observed between lithium and magnesium, further the effect was absent with gold sol which is not hydrated and they suggested that the effect is due to hydration of these ions and of the colloid.

Apart from considerations of hydration there are other possible factors which might account for the so-called antagonistic action of ions. It is usually assumed (though it rests on rather slender evidence cp. Mukherjee, Thesis of Doctorate of Science, University of London, 1921), that the concentrations of different electrolytes which

brings in the same rate of coagulation corresponds to a state of the colloid where the particles have the same density of electrical charge. If that view be correct the observed results might be ascribed to the following causes :—

(1) Difference in the adsorption of the anions and cations present. This is the point of view taken up by Weiser and his collaborators (*J. Phys. Chem.*, 25, 666, 1921), who consider that in the case of colloidal solutions of arsenious sulphide both the cations and anions are very largely adsorbed. Now in the mixture the anion concentration is higher than in the case of the electrolytes with a divalent cation, and there will be a greater adsorption of the anion. The negative charge on the particles is therefore greater. More cations must therefore be adsorbed to bring down the density of the electrical charge to the value which corresponds to the limiting concentrations. Weiser concludes that the higher coagulating concentration is an index of the greater amount of anion that has been adsorbed.

(2) Freundlich (*Z. Phys. Chem.*, 86, 458, 1914) has pointed out that the adsorbability of one cation may be influenced by the other that is the presence of the univalent cation in comparatively higher concentrations might interfere with the adsorption of the bivalent cation and diminish its coagulating power.

It would seem that a study of the effect of various anions on coagulation by mixed electrolytes with simultaneous determination of the electrical charge will be most useful. The electrical data are essential for a proper understanding of the nature of the effect we are studying. It is to be regretted that there is very little useful data on this subject. In this laboratory a systematic study of the electrical charge is being carried out.

The present paper deals with the effect of various

anions on coagulation of arsenious sulphide hydrosol by mixed electrolytes.\*

### EXPERIMENTAL.

During the last few years, a number of papers has been published showing that arsenious sulphide sol has different chemical composition, depending on the methods of preparation.

In our work, we have always adhered to the same method of preparation. The following method has been adopted for determining equi-coagulating concentrations. Light from a single filament lamp is allowed to pass through a layer of definite thickness of the coagulating colloid and the time noted when the sharp outline of the filament disappears. The intensity of the light is kept constant by passing a definite current through the filament. Electrolytes are considered to have equi-coagulating concentrations when the time required for reaching the same stage of coalescence is the same in each case. For each pair of electrolytes used the mixtures as well as the individual electrolytes are exactly equi-coagulating. During an experiment the colloid is tested from time to time by determining the coagulating concentration of a particular electrolyte.

TABLE I.

% Concentration of Sodium Benzoate.	% Concentra- tion of Barium Chloride.	Sum.	% Concentra- tion of Calci- um Bromide.	Sum.	% Concentration of Calcium Benzoate	Sum.
0	100	100	100	100	100	100
20	134	154	159	179	175	195
38	138	171	179	212	190	223
50	130	180	170	220	180	230
66	100	166	141	207	146	212

\* Since this work was finished Weiser has published another paper on adsorption by precipitates (J. Phys. Chem., 28, 237, 1924).



% Concentration of Sodium benzoate.	% Concentration of Magnesium chloride.	Sum.	% Concentration of Barium benzoate.	Sum.
0	100	100	100	100
20	182	202	150	170
33	203	236		
50	195	245	150	200
66	155	221	120	186

Coagulating concentration of Sodium benzoate mean—0.17 N\* = 100

"	"	"	Barium chloride—0.0015 N = 100
"	"	"	Calcium bromide—0.0017 N = 100
"	"	"	Calcium benzoate—0.0018 N = 100
"	"	"	Magnesium chloride—0.002 N = 100
"	"	"	Barium benzoate—0.0014 N = 100

TABLE II.

% Concentration of Sodium benzoate.	% Concentration of Potassium chloride.	Sum.	% Concentration of Lithium chloride.	Sum.
0	100	100	100	100
20	121	141	181	201
33	114	147	169	202
50	86	136	136	186
66	62	128	98	164

Coagulating concentration of sodium benzoate—0.16 N = 100

"	"	"	Potassium chloride—0.06 N = 100
"	"	"	Lithium chloride—0.08 N = 100

\* The sum of cations given in the tables is the sum of the percentage concentration of each cation taking the coagulating concentration of each separately to be hundred.

The actual values for different pairs varied respectively from 0.166 N to 0.174 N. The difference in the coagulating concentrations of barium chloride and barium benzoate may be due to experimental errors. But nothing definite can be said until they are more carefully examined. The barium benzoate was prepared from baryta and benzoic acid.

Percentage concentration of sodium benzoate.	Percentage concentration of sodium chloride.	Sum.
0	100	100
20	141	161
33	125	158
50		
66	98	164

Coagulating concentration of sodium benzoate—0.18 N=100

„ „ „ sodium chloride—0.08 N=100

TABLE III.

% Concentration of sodium chloride.	% Concentration of barium chloride.	Sum.	% Concentration of calcium bromide.	Sum.	% Concentration of Magnesium chloride.	Sum.
0	100	100	100	100	100	100
20	134	154	138	158	135	155
33					135	168
50	115	165	125	175	125	175
66	80	146	94	160	104	170

Coagulating concentration of sodium chloride (mean)—0.075 N\*=100

„ „ „ Barium chloride—0.00155 N=100

„ „ „ Calcium bromide—0.0017 N=100

„ „ „ Magnesium chloride—0.002 N=100

TABLE IV.

% Concentration of sodium acetate.	% Concentration of Barium acetate	Sum.	% Concentration of Barium chloride.	Sum.	% Concentration of Magnesium chloride.	Sum.
0	100	100	100	100	100	100
20	164	184	156	176	210	230
33	176	209	158	191	233	266
50	170	220	138	188	229	279
66	130	196	125	191	175	241

The actual values varied from 0.073 N to 0.078 N for different pairs.

Coagulating concentration of sodium acetate (mean)—0.19 N\*—100

" " " Barium chloride—0.0015 N=100

" " " Barium acetate (approx.)—0.0014 N=100

" " " Magnesium chloride—0.0019 N=100

Percentage concentration of sodium acetate.	Percentage concentration of calcium bromide.	Sum.	Percentage concentration of sodium chloride.	Sum.
0	100	100	100	100
20	191	211	178	198
33	208	241	155	188
50	204	254	121	171
66	174	240	85	151

Coagulating concentration of sodium acetate—0.18 N=100

" " " Calcium bromide—0.0016 N=100

" " " Sodium chloride—0.07 N=100

TABLE V.

Percentage concentration of Potassium Trichlor-acetate.	Percentage concentration of Barium Trichlor-acetate.	Sum.	Percentage concentration of Trichlor-acetic acid.	Percentage concentration of Barium Trichlor-acetate.	Sum.
0	100	100	0	100	100
20	123	143	20	108	128
50	100	150	33	104	137
66	85	151	66	65	131

Coagulating concentration of Trichlor-acetic acid—0.04N=100

" " " Barium Trichlor acetate—0.00156N=100

" " " Potassium Trichlor-acetate—0.09N=100

Percentage concentration of Barium benzoate.	Percentage concentration Barium chloride.	Sum.	Percentage concentration of $K_4Fe(CN)_6$ .	Percentage concentration of KCl.	Sum.
0	100	100	0	100	100
20	78	98	20	105	125
33	64	97	33	93	126
50	49	99	50	81	131
66	33	99	66	53	119

\* The actual values varied from 0.187 N to 0.195 N for different pairs.

Coagulating concentration of Barium berzoate—0.0014 N=100

" " " Barium chloride—0.0015 N=100

" " "  $K_4 F_6 (CN)_6$  —0.2 N=100

" " " KCl —0.07 N=100

Percentage coagulating concentration of LiCl.	Percentage coagulating concentration of Mg Cl <sub>2</sub> *
0	100
25	200
50	220
73	233

## DISCUSSION.

In their experiments neither Freundlich nor Weiser has used electrolytes other than chlorides. The question how far the adsorption of anions is responsible for the increase in the coagulating concentrations of the divalent cations remains open. They have used mixtures of electrolytes containing two cations. It has been shown by Weiser (J. Phys. Chem., 28, 1924, 241) that there is a displacement of adsorption of one cation by the other. It is therefore not clear whether the observed effect is to be attributed at least in part to the adsorption of anions or to some factor other than the adsorption of anions. If however the mixture of electrolyte contain only one cation and an increased concentration of the cation is necessary for the mixture we must conclude that anion adsorption is responsible for the effect. We have such an instance in the effect of sodium benzoate and sodium acetate on the coagulating concentration of sodium chloride. Displacement of adsorption of one cation by another is impossible since we have got only one cation.

It will be noted that sodium acetate increases the coagulating concentration of sodium chloride almost to

\* The data for the pair LiCl and MgCl<sub>2</sub> are taken from Freundlich's *Kapillarchemie*, p. 684 (1922), and added for comparison only.

the same extent as it does in the case of barium chloride. Similarly sodium benzoate has almost equal effects on sodium chloride and barium chloride. So we conclude that even in cases where the displacement of adsorption of one cation by another is not possible the effect of the anion is as pronounced as in the case where displacement of adsorption may occur in addition.

TABLE VI.

Percentage concentration of Lithium Chloride.	Percentage * concentration of Barium Chloride.	Percentage concentration of Sodium Acetate.	Percentage concentration of Barium Chloride.	Percentage concentration of Sodium Chloride.
0	100	0	100	100
25	133	20	156	178
50	110	33	158	155
73	110	50	138	121
		66	125	85

It is therefore difficult to say whether the effects of sodium acetate on Barium chloride is due to the displacement of the adsorption of  $\text{Ba}^{++}$  ion or simply due to the adsorption of the anion. In a previous paper (Mukherjee and Chaudhuri, J. Chem. Soc., 1924, Vol. 125, p. 795) reasons have been given which indicate that acetate and benzoate ions are more strongly adsorbed than  $\text{Cl}^-$  ion. This observation is in agreement with the observed influence of sodium acetate and sodium benzoate on  $\text{NaCl}$ . The anion adsorption in these cases is therefore clearly established.

Regarding the effect of  $\text{LiCl}$  on  $\text{BaCl}_2$  Weiser has attributed it to the displacement of  $\text{Ba}^{++}$  ion by  $\text{Li}^+$  ion as he has actually observed that the precipitate carries with it

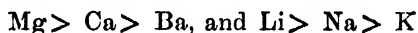
\* The result for the pair  $\text{LiCl}$  and  $\text{BaCl}_2$  are taken from Freundlich's *Kapillar-chemie*, p. 634 (1922).

less Ba in the presence of LiCl than in its absence. It is however necessary to point out that this observation in itself does not justify Weiser's conclusion. Apart from the difficulties of interpreting analytical data on adsorption (cp. W. O. Ostwald *Koll-Z.* 30 (1919), 279), Weiser's observation only shows that a smaller number of barium ions are present in the "double layer." It does not follow that there is also a smaller number of barium ions fixed on the surface than in the other case. The distinction between the adsorbed ions which are free to move under an impressed electrical field and those which are not free to move has been overlooked. The relative ratio of the two cations per unit surface in the fixed layer of ions which really determine the diminution in the electrical charge is not necessarily identical with that in the freely moving second sheet of the Helmholtz double layer. Analytical data cannot evidently give an idea of the distribution in either layer. It gives the idea of the total effect due to both layers assuming that the adsorption of the solvent is negligible. Weiser's interpretation will be true if coagulation takes place when the particles are practically neutral as in that case there will be no freely moving ions and all the cations are fixed on the surface. There is no justification for such an assumption.

We would now point out that in all these cases the assumption of a small adsorption of an anion will be sufficient to explain the observed effects\* without recourse being had either to considerations of hydration or to displacement of adsorption. If we consider the experiments of Ellis, Powis and Kruyt at low concentrations of the electrolyte we find that there is in most cases a slight rise in the negative charge when the electrolyte is KCl or LiCl. We see that in the case of a chloride with a cation

\* Of course we cannot say that this is actually the case in the absence of relevant data on the electrical charge.

of low coagulating power the increase in the charge may be more pronounced (cp. the curves given by Freundlich *Kapillarchemie*,\* page 354, 2nd edition). In that case there ought to be a gradation in the effects of electrolytes having common anion and cations of same valency but different coagulating power. The coagulating power of lithium is the weakest among the alkali metal ions and that of magnesium among the divalent cations Ba, Sr, Ca, Mg, etc. Both Freundlich and Weiser have observed that lithium and magnesium show the most pronounced effect. Our experiments also support this observation as will appear from the data given above. Where the anions are adsorbed to a marked extent the greater increase in the negative charge is reflected in a greater difference in the coagulating concentrations of different cations of the same valency. We notice that the influence of sodium benzoate is in the order



that is the reverse order of their precipitating power. If we now contrast the effect of mixing sodium chloride instead of sodium acetate or sodium benzoate we find that the individual variations between barium chloride, calcium bromide and magnesium chloride are scarcely perceptible. If the displacement of adsorption of these cations varied from one to another one would then have expected a greater difference between them. Magnesium in no way shows characteristic difference compared to barium or calcium. The anion adsorption in the case of

\* If similarly in the case of arsenious sulphide there is an increase in the charge at low concentration of these chlorides then it is not necessary to assume either hydration or the displacement of adsorption. In collaboration with Mr. S. G. Chaudhuri measurements are being made on the variation in the rate of cataphoresis of Arsenious sulphide particles with the change in concentration of acids. So far HCl and H<sub>2</sub>SO<sub>4</sub> have been studied. The variation in charge is very complicated and depends probably on whether we are dealing with an orange or yellow sol. on the concentration of H<sub>2</sub>S and probably on the reaction between H ion and the stabilising ion adsorbed on the surface of the colloid.

the chlorides is less pronounced because we are dealing with a relatively less adsorbable anion and cations with fairly strong coagulating power. Our contention is that it is the initial rise in charge at low electrolyte concentration which is to a large extent responsible for all these effects. It does not matter whether the increase in charge is due to a strong adsorption of the anion or to a weak adsorption of the cation as in the case of sodium benzoate and lithium chloride respectively. Recognising that on the addition of a small quantity of an electrolyte (say up to 66% of its coagulating concentration) there is an increase in the charge, the protecting effect of such an increase will of course be more prominent if the coagulating cation has a weaker precipitating power. That is why we find so great an effect of lithium chloride on magnesium chloride or of sodium benzoate or sodium acetate on magnesium chloride. The effect of sodium acetate on calcium bromide is not in any way less pronounced than that of lithium chloride on magnesium chloride and the effect of sodium benzoate on lithium chloride is fairly comparable to that of lithium chloride on magnesium chloride.

Similarly potassium trichloracetate has a greater effect than the acid on the coagulating concentration of the barium salt in keeping with the lower coagulating power of the potassium ion compared to that of the hydrogen ion. The pair barium benzoate and barium chloride show a marked contrast to sodium benzoate and sodium chloride. The total barium ion concentration remains fairly constant. Whereas in the case of sodium acetate and sodium chloride the total sodium ion concentration becomes more than double the coagulating concentration of sodium ions when only sodium chloride is used. The difference is probably due to the low anion concentration of the barium salts and the greater coagulating power of



the barium ion. There ought to be from our point of view no increase of charge at low concentration of barium salts. The curves of Ellis and Powis show this peculiarity. Potassium ferrocyanide and potassium chloride on the other hand show a weaker effect than sodium acetate and sodium chloride. This is probably due to the greater coagulating power of potassium ion on the one hand and the weaker adsorption of  $\text{Fe}(\text{CN})_6$  ion on the other hand in spite of its higher valency as shewn in a previous paper.

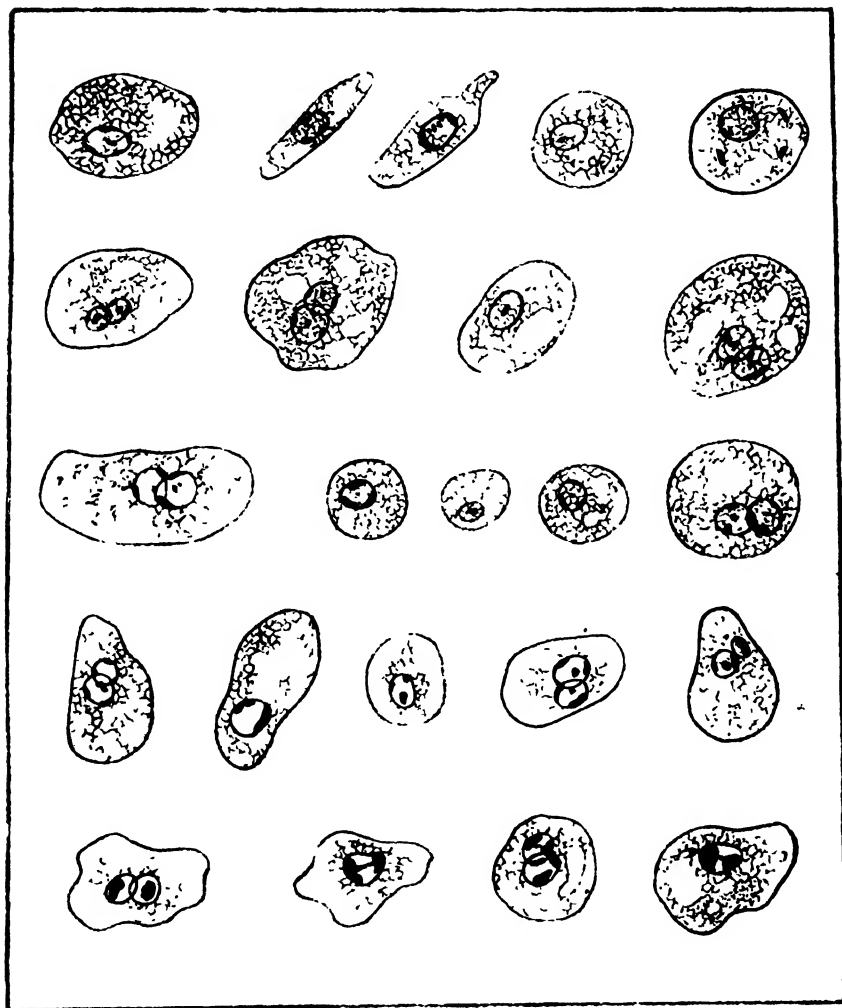
We would again repeat that in order to clearly understand the nature of these effects the corresponding measurements of the charge is absolutely necessary and discussion on the displacement of adsorption might be profitably postponed till we have obtained the necessary data.

Lastly we would make a few observations on ionic antagonism as observed in nature. It is rather rash to draw conclusions from a few experiments on coagulation in the laboratory and to conclude from the similarity of effects that there is a similarity in the cause. At the same time we might suggest that at least one of the main causes which is responsible for ionic antagonism as observed by Lillie, Osterhout, Loeb and Clowes (J. Phys. Chem., 20, 1916) is the effect of the ions on the electrical charge of the dispersed system. The similarity in the effects is probably to be attributed to this common factor. Clowes states "whatever the ultimate theoretical interpretation may be the close correspondence between data accumulated in such widely diversified fields affords substantial evidence of the existence of some heretofore unappreciated fundamental physical principle" and this fundamental physical factor might be the electrical charge.

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# ZOOLOGY



# ON THE NUCLEAR STRUCTURE OF THE AMOEBA OF LIVER ABSCESS.

By

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Recently there has been a good deal of controversy regarding the distinction between *Amoeba histolytica* and *Amoeba coli* being based on the number of nuclei in the cystic stage. Several observers, such as SWELLENGREBEL and KUENEN, have observed eight nuclei in the cysts of *A. histolytica*. This has been explained by some as an abnormality and not the rule, the four-nucleated cyst being characteristic of *A. histolytica*. KNOWLES and COLE have, as a result of examination of a large number of stools of dysentery cases, expressed their opinion in definite terms, namely, that eight-nuclei cysts are more often found in the true *Amoeba histolytica*, so that they have raised doubts regarding the distinction between these two species of Amoeba. BRUG has critically reviewed their paper and has expressed the view that the writers have fallen into error on account of the dysentery cases stools which they examined being not cases of amoebic, but bacillary dysentery, the amoeba found in the stools being *A. coli* and not *A. histolytica*. This accounts for their getting eight-nucleated instead of four-nucleated cysts; therefore the distinction between the cysts of *A. histolytica* and *A. coli* holds good, although in some exceptional cases *A. histolytica* may show eight nuclei. He calls in question the propriety of the complicated staining methods followed by the above observers, which led them into error. Recently the writer had an opportunity of studying the structure of the amoeba from an unopened liver abscess, in which the amoebae, besides present in exceptionally large numbers, showed some peculiarities not hitherto observed and which I think are worth recording. The observers who have studied amoebae found in liver abscesses are all agreed in that they have found always only one form of amoeba—noncystic, undivided, amoeboid forms. In this connection, it is not necessary to refer to the observations of MARTIN and LISTON, as they have been dealing with *Amoeba Limax*, and

not *Amoeba histolytica*, which species they thought they had cultivated from liver abscess pus. Noc had asserted that he never found cysts in liver abscess pus.

The writer obtained the material for his observations by scraping the wall of an unopened liver abscess, a few hours after the death of the patient. The abscess was a single one; staining for micro-organisms showed no bacilli. Moist cover glass preparation showed innumerable, actively motile amoebae, in most of which red cells could be detected. Clear differentiation between ectosarc and endosarc could be made out. The stained preparation were made in the following way. A thin smear on a slide while moist was immersed in saturated alcoholic picric acid solution to which a few drops of acetic acid had been added. After washing the slide in rectified spirit, it was placed in iron alum solution (rectified spirit 10 parts, 2 parts of 10 p.c. iron alum solution). After an hour the slide was washed in rectified spirit and then immersed in haematin solution (absolute alcohol 20 c.c., 5 gram of haematin) for 2 hours, then differentiated by immersing in iron alum, dehydrated and mounted.

On examining with oil immersion the writer found the amoebae with their characteristic nuclear ring standing out clearly. As each field showed nearly two to three amoebae, it was possible to study their structure with ease. The writer carefully examined five hundred amoebae and made sketches. The following is a résumé of his observations. The amoebae studied can be divided into two classes—one undivided forms and the other dividing forms. The relation between the 1st and 2nd forms is about nine to one. The undivided forms showed the structure of an ordinary *Amoeba histolytica* with a thin cell wall and an excentric nucleus, the latter showing the characteristic structure of the nucleus of *A. histolytica*, a thin ringshaped nuclear wall, circular or oval in shape, with a small caryosome in the middle. Thin strands of chromatic substance were seen between the caryosome and the nuclear wall; the nuclear wall showed irregular condensation or thickening.

The dividing forms do not differ from the above ones in size and general appearance. They are amoeboid. They do not show any thickening or double contouring of the cell wall, so that they can by no means represent the cystic stage. The nucleus shows division into two. The writer has scrutinised hundreds of specimens and examined them by all possible methods. He never found four

nuclei. The two nuclei lie in juxtaposition, often at different levels. In some of the specimens a few thin chromatic blocks were seen, but these are quite unlike the thick black chromatic blocks seen in cysts of *A. histolytica*.

The above observations suggest that the amoeba of liver abscess divides by binary division and no cystic stage intervenes.

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*Baliganj, the 28th August, 1924.*

Fig. 1 shows the amoeba stained by the iron heamatin stain and drawn with 1/12 apochromatic objective and No., 6 eyepiece.

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# NOTE ON TYPHLOPONE FULVA, VAR LABIATA, EMERY, SYN. DORYLUS LABIATUS, SHUCK.

By .

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The genus *Dorylus* included in the genus *Vespa* by Linné in 1764, was founded by Fabricius in 1793 on male specimens only. In 1840 Westwood first figured neuters of *Typhlopone fulva*, the mandibles being depicted as sickle-shaped and serrated on the inner edge and without any prominent teeth. But he gave neither the generic nor the specific description of what he called *Typhlopone fulva*.

Schuckard in his monograph of Dorylidae (1840), gave a description of the workers of *Typhlopone*, but was not aware of the precise relationship between the male *Dorylus* already described and this worker. In 1858 the generic character of the worker of *Typhlopone* was described by Smith, but its position was still not clear. In 1887 Emery showed, in the case of a limited number of species, that the wasplike winged male, huge apterous female and the small blind workers, which had been considered as distinct species, represented the different phases of one and the same species.

In the Fauna of British India (1903) a description of the male and the workers of *Dorylus labiatus* and *Dorylus orientalis* represented in India and of the male, female and the workers of *Dorylus laevigatus* found in Burma and in Borneo and Java are given by Bingham, the female of *Dorylus labiatus* and *Dorylus orientalis* still remaining unknown.

In 1910, in the *Genera Insectorum*, Emery divided the genus *Dorylus* into the following six subgenera, (1) *Dicthadria* Gerstaecker, (2) *Dorylus sensu stricto*, Fabricius, (3) *Anomma* Schuckard, (4) *Typhlopone* Westwood, (5) *Rhogmus*, Schuckard, (6) *Alaopone* Emery, basing his classification on the number of joints of the antenna, the form of the pygidial area, the number and character of teeth on the mandibles. According to this classification *Dorylus labiatus* becomes a synonym of *Typhlopone fulva*, variety *labiata*.



Bingham, in the Fauna of British India in describing the workers of *Dorylus labiatus* makes no mention of the pygidial area and fails to note the difference between the major and minor worker, as regards the terminal portion of the gaster. It may be pointed out that the gaster in the major worker is pale yellow and elongate, being two and half times longer than broad; further, the terminal portion of the fifth segment is shallowly excavated and armed laterally with stout spines (teeth), the middle part of the venter ending in a single tooth, as shown in the figure. In the case of the minor worker the gaster is ovate, one and half times longer than wide, the terminal portion is rounded and shows no excavation nor bears any teeth. Moreover the number of joints of each antenna in the specimens collected by me as well as in specimens identified by Wheeler as *Typhlopone variety labiata* and those labelled as *Dorylus labiatus* in possession of the Indian Museum are identical in all respects; there are eleven joints both in the major and minor workers instead of eleven joints and ten joints in major and minor workers respectively, as recorded by Bingham in the Fauna of British India.

In both cases the antennae are geniculate and nearly as long as the head. The scape is smooth, less than half of the flagellum; the flagellum is covered with pubescence and consists of ten sub-equal joints, all the joints except the first and the last being wider than long and the terminal joint being sub-clavate.

There is not much difference as regards the mandible between the major and minor workers.

The length of the major and the minor worker is given in the Fauna of British India as 6.8 mm. and 2.5-4 mm. respectively, but in my collection the length varies from 10.5 mm. to 4 mm., there being no sharp line of demarcation; the minor worker is only comparatively smaller in size and paler in colour.

*Dorylus labiatus* is fairly distributed over the whole continent of India. But nothing is known about its ethology. Woodmason once reported the workers from Calcutta, and Rothney found a nest under a large stone at the bottom of a tank near Barrackpore. But no further details are given by them. Males are quite common in Calcutta and several of them were caught by me at night during the cold season. The workers are very scarce, probably due to their subterranean habit, and it is interesting from the point of view of local distribution to note that only once during the last rainy season I came early in the morning across a group of nearly

fifty blind workers helplessly crowded together in the shady corner of a damp and ill-lighted room of my Calcutta house. The place was situated near the mouth of a gutter which opened toward the outside of the room on to the pavement of the yard. As there was no soft ground within a radius of fifty yards of the place to cover their march, it was likely that the ants had come out from the wall beneath the gutter itself. Phediole ants were seen marching out in files on the other side of the wall away from the gutter, probably because their nest was occupied by the "drivers" or because they had been frightened somehow or other. The workers when handled in the live condition emitted a bad smell.

Before concluding I like to take this opportunity of conveying my thanks to the officers of the Zoological Survey of the Indian Museum for their kind permission to use the Museum and the library and to Dr. P. Brühl for going over my manuscript.

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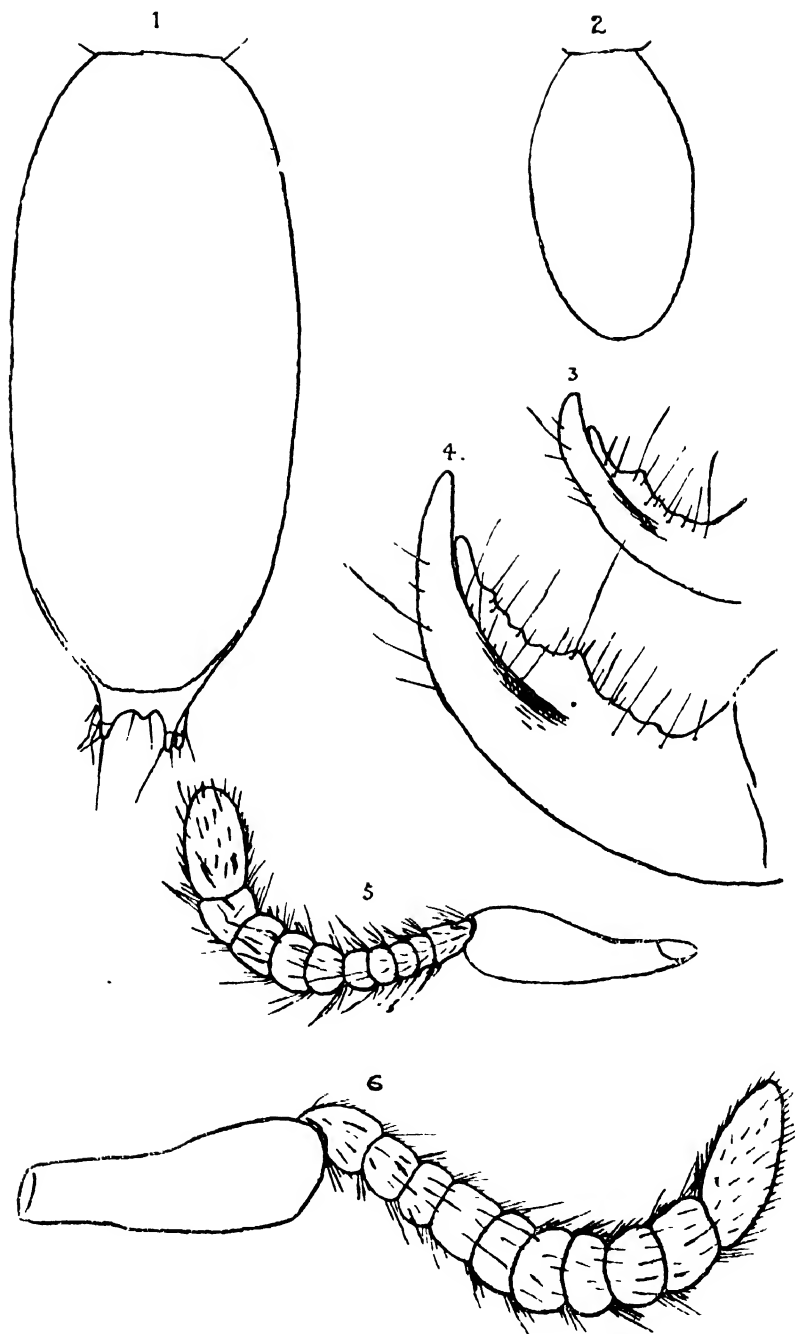
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## EXPLANATION OF FIGURES.

## PLATE I.

1. Gaster of the major worker     $\times 15$ .
  2. Gaster of the minor worker     $\times 15$ .
  3. Mandible of the minor worker  $\times 40$ .
  4. Mandible of the major worker  $\times 40$ .
  5. Antenna of the minor worker     $\times 40$ .
  6. Antenna of the major worker     $\times 40$ .
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# **BOTANY**



# ROAD SLIMES OF CALCUTTA

By

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Probably many of the people living in the Plains of India have made the acquaintance with road slimes, the experience not having been exactly of an agreeable nature. It is therefore a matter of some interest to discover the culprits which often are the cause of people slipping or falling when passing along roads or pathways during the rainy season or being practically prevented from proceeding when trying to cross a grass plot after a shower of rain.

The organisms which are the cause of the formation of those slimy masses belong to the Myxophyceae or blue-green algae. The colour of the road slimes, however, are far from being usually bluish-green; their colour being more commonly brown, blackish-green, olive-green, dirty-green, bluish-green, pale-green or yellow-green or colourless. Similarly, their shape, size, mode of growth, their degree of toughness, tenacity, and gelatinousness varies within wide limits, according to the condition in which they live. Thus they may be spherical, elliptical, oblong, tuberous, they may form layer after layer, or cushion-like aggregations or thinner or thicker membranes, or irregular or amorphous mucous masses and so on. As to their consistency, they may be hard and tough like leather or they may be soft and yielding like a mass of gelatine; some may be transparent, others may be more or less opaque.

As is well-known, the Myxophyceae concerned in the formation of road slimes possess great resisting powers, enabling them to tide over periods of drought accompanied by low or high temperatures. As may be expected, their growth is most vigorous during the rainy season, that is to say, in Calcutta from the middle of June to the end of September, though Nor'westers in April or May and belated monsoon showers in October will also cause their appearance.

With the beginning of the dry seasons they shrivel up, the mucous envelope losing most of its absorbed water; but the algal cells or filaments being encased in the hardened mucus manage to escape with



their life, or at least a good number of them, although the dried-up road slimes, which here and there can yet be spotted as brownish or blackish patches or may remain entangled among the haulms of grasses, are trampled upon, scraped off, mixed with dust or otherwise maltreated. Here and there the road slimes, such as those containing *Microcoleus paludosus* or *Nostoc Communis*, in drying, often form thin sheets, which gradually are ground down by people stepping on them, and after being reduced to powder they are distributed either by the wind or as part of road sweepings and in other such ways.

An interesting observation was made by the writer in the course of last year. For a certain other purpose a large earthenware vessel full of garden earth was kept on the terrace of the botanical laboratory during the month of May, the soil being occasionally watered. At the end of a few weeks some isolated filaments of *Microcoleus paludosus*, *Lyngbya aerugineo-coerulea* and *Oscillatoria tenuis* made their appearance. Soon after, they formed a thin film of blue-green colour over the whole surface of the vessel intermixed with more or less spherical patches of grayish blue and pale brown mucus from 1 mm to 10 mm in diameter which finally formed a thick membrane of slime here and there, where there was a sufficient quantity of water. They were allowed to grow there up to the month of August, when the whole surface was partly covered up by a slimy mass of *Aphanocapsa brunea*, and a thin felt, about .5 mm to 1.5 mm thick, of *Microcoleus paludosus* and a few filaments of *Oscillatoria tenuis* and *Lyngbya aerugineo-coerulea*. In September they were allowed to dry up and in the first week of November there was hardly any trace of those plants except some brown or gray patches which could hardly be distinguished from the dry soil, and they did not show anything particular under the microscope. But after about half an inch of water had collected over the soil owing to a heavy shower of rain in the night of the 19th November, 1923, the plants, after 12 hours, had developed into a slimy mass and were growing as luxuriantly as before.

The regenerative power of the plants is so great that they do not take more than a few seconds to recover and multiply. They can also withstand considerably higher temperatures. For instance, a quantity of slime was placed on a slide and exposed to a temperature of 40°C; the slime, which contained *Aphanocapsa brunea*, *Oscillatoria amphibia*, *Oscillatoria tenuis*, and *Phormidium tenue*, after drying showed under the microscope only faint outlines of *Aphanocapsa brunea* in a brownish-

grey sheath. But as soon as a drop of water was allowed to penetrate under the cover glass, the cells began to assume a healthy appearance, and within 5 minutes all the cells of *Aphanocapsa brunea* began to divide as rapidly as before; the slimy envelope swelled up as before, absorbing the drop of water. The slime was further exposed to higher degrees of temperatures and at 60°C *Oscillatoria amphibia* became yellow, the cells of the filaments separated from one another and the plant had evidently died. *Oscillatoria tennis* and *Aphanocapsa brunea* also had met with the same fate.

The sheaths of none of those plants showed the cellulose reaction with chloro-zinc-iodine, but the sheath of *Scytonema mirabilis* became beautifully blue when treated with chloro-zinc-iodide for about 15 minutes; but the contents of the sheaths contracted and became brown.

These slimes are insoluble in formalin alcohol, ether and carbon bisulphide; but they swell up, dissolve or become gelatinous when soaked in water. The best stains for these slime-algae proved to be anilin blue and haematoxylin.

The plants that are found in these slimes are:

1. *APHANOCAPSA BRUNEA* Naeg.

This plant, as it occurs in the road slimes of Calcutta, is very variable. The colour of the slime is blackish brown, brown, greenish-brown, or grayish-green and rarely colourless and transparent. The slime of this algae often contains *Chroococcus turgidus*, *Chroococcus minutus*, *Oscillatoria tennis*, occurring as scattered solitary filaments, *Oscillatoria amphibia*, present in large numbers as bundles of filaments, fine threads of *Phormidium tenue* and a few species of *Diatoms*. The cells are spherical or slightly oblong, especially when on the point of dividing, 4-10  $\mu$  by 4-6  $\mu$ , the contents being granular, brownish-green or blue-green. This species is also described in *Commentationes algologicae* II, "Indian Bark Algae," p. 2.

2. *APHANOCAPSA GREVILLEI* (Hass.) Rabenhorst.

Plant-mass dirty green, forming small protuberances on moist soil, gelatinous; cells spherical, 3-4  $\mu$  in diameter; contents granular and blue-green. This species is also found in Bengal filter beds. See *Com. Algol.* I, "The Algae of Bengal filter beds," p. 3.

3. *GLOEOCAPSA QUATERNATA* (Brebisson) Kuetzing.

Plant-mass consisting of small tubercles on moist soil, dirty-green; cells spherical, in twos, fours, eights or more in each family; sheaths

distinct, lamellae 3 or more in number,  $6\ \mu$  in diameter without the sheath,  $8\ \mu$  with the sheath, sheath  $2\ \mu$  thick, contents granular and blue-green. Associated with this are found *Chroococous turgidus* and *Chroococcus minutus* in large numbers. See also Com. Algal., II, "The Algae of Bengal filter beds," p. 3.

#### 4. CHROOCOCCUS TURGIDUS (Kuetzing) Naegeli.

Plants not forming a stratum, associated with *Gloeocapsa quaternata* and *Aphanocapsa brunea*, solitary or in twos, rarely in fours; cells more or less angular, sheaths transparent, rather indistinct, contents granular, bluish-black. See Com. Algal. I, "The Algae of Bengal filter beds," p. 2, Com. Algal., II, "Indian Bark Algae," p. 1.

#### 5. CHROOCOCCUS MINUTUS (Kuetzing) Naegeli.

Plant-mass not forming a stratum, individuals solitary or in twos or fours, present in large numbers with *Gloeocapsa quaternata* and in small numbers with *Aphanocapsa brunea*. Plants  $9-15\ \mu$  by  $6-15\ \mu$ , cells  $3-5\ \mu$  in diameter, angular by mutual pressure; contents granular rather bluish-black; sheaths hyaline, rather indistinct. See Com. Algal., II, "Indian Bark Algae," p. 1.

#### 6. OSCILLATORIA PRINCEPS Vaucher.

Plant-mass forming black, thin membranes on muddy soil; trichomes  $16-18\ \mu$  in diameter, straight, rigid, fragile, lying somewhat parallel to one another, not constricted at the joints, slightly tapering, more or less curved and truncate at the apex, somewhat capitate, apical cell convex above; calyptra none; cells 4-6 times shorter than wide, about  $3-0\ \mu$  in length, transverse walls not granulated; cell contents granular, blue-green. On the roads—Woodburn park; Coll., 23-8-1923. De Toni—Myxophycese, p. 150, Minnesota Algae, pp. 58, 62.

#### 7. OSCILLATORIA TENUIS Agardh.

Plant-mass forming a thin, rather blackish brown membrane on roads and moist soil, the filaments being often found associated with other algae and almost always present in the slimes. They are either brown or blue-green or deep verdigris-green. As regards its other characters they are similar to those described in "The Algae of Bengal filter beds," p. 6.

#### 8. OSCILLATORIA AMPHIBIA Agardh.

The plant is found commonly as separate bunches of filaments lying parallel to one another, or as solitary filaments scattered here and there or rarely entangled in circinate fashion like *Arthrospira*

*tennis* Brühl et Biswas, embedded in the slimes especially of *Aphanocapsa bruneu*. Sometimes it forms a deep verdigris-green pure stratum of its own on damp muddy soil or on grassy plots, other characters being the same as described in "Com. Algol., I, The Algae of Bengal filter beds," p. 4.

9. *OSCILLATORIA CALCUTTENSIS* Biswas, *sp. nova*.

Strato bruneo, membranaceo, filamentis in fasciculos parallelos aggregatis; trichomatibus elongatis, rectis, ad genicula hand constrictis,  $2\ \mu$  crassis, apice breviter attenuatis, acutissime acuminate, hand capitatis, sed uncinatis vel tertuosis; articulis diametro trichomatis 2-5—plo longioribus, 6-10  $\mu$  longis, dissepimentis utroque latere granulis tribus instructis; contentu aerugineo-coeruleo, sparse granuloso.

Plant-mass brownish, consisting of bundles of aggregated filaments arranged parallel to one another; trichomes long, tenuous, showing vigorous oscillating movements, not constricted at the joints,  $2\ \mu$  in width, apex of trichome gradually tapering, ending acuminate in a sharp point, twisted, not capitate; apical cell mucronate, calyptra none; cells 3-5 times as long as broad, 6-10  $\mu$  long, transverse walls marked by 3 granules arranged in rows on either side; cell contents sparsely granular, blue-green.

*Oscillatoria acuminata* Gomont differs from this species by the plant-mass being blue-green in colour, trichomes 3-5  $\mu$  in diameter, slightly constricted at the joints; cells 5.5-8  $\mu$  in length, transverse walls not marked by three well defined granules and the entire cell contents being filled up with granules.

10. *OSCILLATORIA ANIMALIS* Agardh.

Plant-mass forming a deep blue-green, rather slimy coating on soil; trichomes 3-4  $\mu$  in diameter, showing movements, short-tapering acute at the apex, not capitate, calyptra none; cells 2-4  $\mu$  in length, subquadrate, transverse walls here and there granulated; cell contents granular, blue-green.

Collected from the roads and moist soil, Calcutta, August, 1922-23. De Toni, pp. 178-179, Minnesota Algae, pp. 79, 60.

11. *OSCILLATORIA QUADRIPUNCTULATA* Brühl et Biswas.

Found on the road near the west-gate of the College compound, Baliganj, on the 25th July, 1922, as a verdigris-green stratum; other characters are similar to those described in "The Algae of Bengal filter beds," p. 5.

12. *OSCILLATORIA ACULA* Brühl et Biswas.

Observed as solitary filaments in the algae of the road slimes. For description, see "Com. Algol., II, Indian Bark Algae," p. 3.

13. *PHORMIDIUM TENUE* (Meneghini) Gomont.

Found abundantly in the slimes of *Aphanocapsa brunea*, and *Gloeocapsa quaternata*. For description, "see Com. Algol., I, The Algae of Bengal filter beds," p. 8.

14. *LYNGBYA AERUGINEO-COERULEA* (Kuetzing) Gomont.

Very commonly associated with the other algae of road slimes or forming a pure blue green membrane on grassy plots or damp soil. For description, see "Com. Algol., II, Indian Bark Algae," p. 10.

15. *MICROCOLEUS PALUDOSUS* (Kuetzing) Gomont.

Plant-mass membranaceous, about 0.5-1.5 mm. in thickness, blue-green or greenish-black when dry; filaments simple, twisted, or forked, often associated with other algae; sheaths moderately mucous, thickness variable, open at the apex or closed or rather pointed, hyaline, and not stained by chlorozinc-iodine; trichomes 3-7  $\mu$  in diameter, not constricted at the joints, parallel, straight or twisted into cords, rather gradually tapering at the apex, end-cell subacute or acute, not capitate; cells almost twice as long as broad, 4-10  $\mu$  in length, partition walls not granulated; cell contents granular, blue-green.—Collected from the roads of Woodburn Park, 23. 8. 23.; growing profusely in an earthenware vessel on soil, Baliganj Laboratory—July-August-November, 1923; Baliganj nursery on damp soil—September, 1922; on grassy lands in Bhowanipur—August, 1922 and 1923. De Toni Myxophyceae, p. 376.—Minnesota Algae, pp. 155, 158.

16. *NOSTOC COMMUNE* Vaucher.

Colony gelatinous, firm, at first spherical, afterwards becoming flattened, finally spreading out into undulating folded, fleshy or membranaceous, entire or ragged, often perforated sheets; leathery, on the surface blue-green or olive in colour; filaments flexuous, entangled; sheath bluish green near the surface of the mass, in the interior more or less distinct, often colourless; trichomes 4-6  $\mu$  in diameter; cells depressed-spherical or barrel-shaped 4-6  $\mu$  in length; heterocysts more or less spherical, 6-8  $\mu$  in diameter, intercalary, gonidia or spores oblong, distant from the heterocysts, not in chains, 8-12  $\mu$  by 6-8  $\mu$  wall of gonidia smooth and hyaline; cell contents granular, blue-green.

Collected from the roads of Woodburn Park, 23. 8. 23. De Toni, Myxophyceae, p. 404. Minnesota Algae, pp. 163, 171-173.

17. *NOSTOC SPHAERICUM* Vaucher.

Colonies at first spherical, varying for 1 mm. to 15 mm. in diameter, but finally irregularly tuberculate, thick, solid, deep brown in colour; filaments flexuous, densely entangled, embedded in a firm, thick brown sheath; trichomes  $4\ \mu$  in width; cells spherical or oblong or square,  $4-6\ \mu$ , in length; heterocysts  $6-8\ \mu$  by  $4-6\ \mu$ , the spherical ones  $4-8\ \mu$  in diameter; gonidia oval or oblong  $6-8\ \mu$  by  $4-6\ \mu$ , epispore of gonidia smooth; cell-contents blue-green, finely granular; contents of gonidia gonidium coarsely granular blue green.

Collected from the roads in Bhowanipore, Calcutta, 21. 8. 1923 De Toni, Myxophyceae, p. 409; Minnesota Algae, pp. 163, 171-173.

18. *CYLINDROSPERMUM BENGALENSE* BISWAS, *sp. nova*.

Strato expanso, viridi-aerugineo, membranaceo, trichomatibus  $3-4\ \mu$  crassis, sinuosis, elongatis, fragilibus, adgeniculis constrictis, intricatis; cellulis saepius rectangularibus, oblongis  $3-8\ \mu$  longis; dissepimentis granulis haud obsitis; heterocystis terminalibus, hastiformibus, basi latoribus,  $6-8\ \mu$  longis, basi  $3-4\ \mu$  latis, apice subacutis; sporis ellipsoideis vel elliptico-oblongis,  $12-21\ \mu$  longis,  $6-10\ \mu$  latis, episporio laevi, hyalino; contentu cellularum granuloso, aerugineo.

Hab, ad terram humidam in viis nemoris Woodburn Park dicti.

Lectum 23. 8. 1923.

Stratum expanded, thin, membranaceous; trichomes  $3-4\ \mu$  in width, elongated, more or less fragile, sinuous, constricted at the joints, but not torulose, intricate; cells often rectangular or oblong, not granulated at the partition walls,  $4-6\ \mu$  in length; heterocysts terminal, never at both ends, lance-shaped, flat at the base, subacute at the apices,  $6-8\ \mu$  by  $3-4\ \mu$  at the broadest part; spores elliptical or oblong  $12-24\ \mu$  by  $6-10\ \mu$ ; epispore smooth hyaline; contents coarsely granular, blue-green.

Collected from the roads of the Woodburn Park, 23. 8. 1923.

This species is close to *Cylindrospermum tropicum*, which differs by the heterocysts being twice as thick as the vegetative cells and the spores being up to  $43\ \mu$  long; *Cylindrospermum Goetzei*, differs by the plant not forming a membrane, cells being torulose, spores minutely punctate, yellowish brown; *Cylindrospermum doryphorum* Brühl et Biswas, is very brittle, the filaments floating freely in

water, heterocysts either at one or both ends of the trichome, cells slightly or not at all constricted at the joints, 4-8  $\mu$  by 2-4  $\mu$ ; a peripheral zone and the dissepiments are hyaline, resting spores 8-12  $\mu$  by 4-6  $\mu$ ; *Cylindrospermum minutissimum* has cylindrically oblong heterocysts and its spores are 18-20  $\mu$ ; *Cylindrospermum humicola* has globose heterocysts.

19. SCYTONEMA MIRABILIS (Dillwyn) Bornet.

The plant is very frequent in and about Calcutta occurring as blackish green felty expanded and cushion-like spongy masses on roads, covering a considerable part of the road and very commonly associated with other road-slime algae. The sheath is brown and lamellose and is stained blue when treated with chloro-zinc-iodine.

For description see "Com. Algol. II Indian bark algae," pp. 14-15.

When a sufficient quantity of water accumulates, other green small plant organisms are found associated with them; such as, *Cosmarium granatum* Breb., *Scenedesmus obtusus* Meyen., *Scenedesmus quadricauda* Meyen, *Closterium* sp., *Eudorina* sp. and some others.

A few species of *Diatoms* are also almost always present in the road slimes, and the brown colour of the latter is in some cases due to the presence of these diatoms in large numbers.

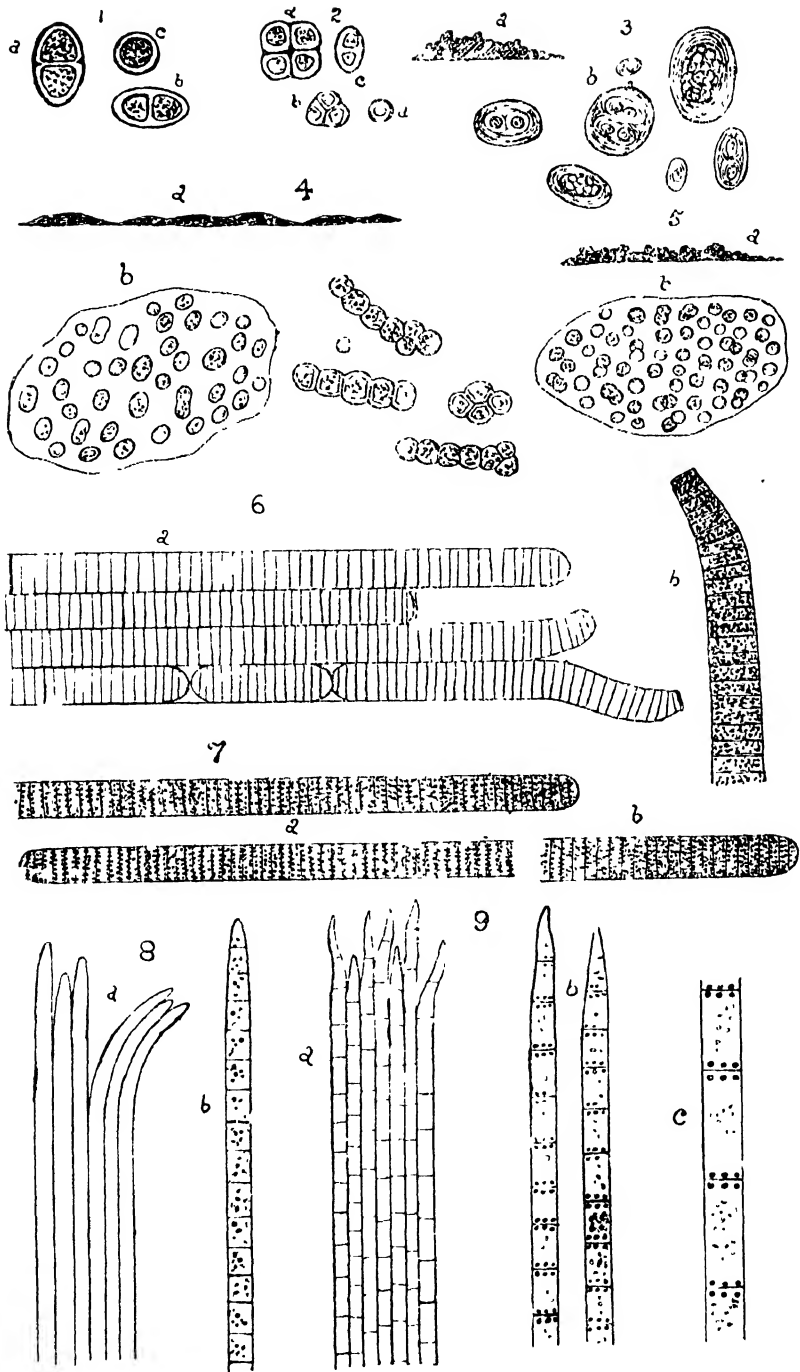
BOTANICAL LABORATORY,

UNIVERSITY COLLEGE OF SCIENCE,

Baliganj, Calcutta, the 28th August, 1921.







## EXPLANATION OF FIGURES.

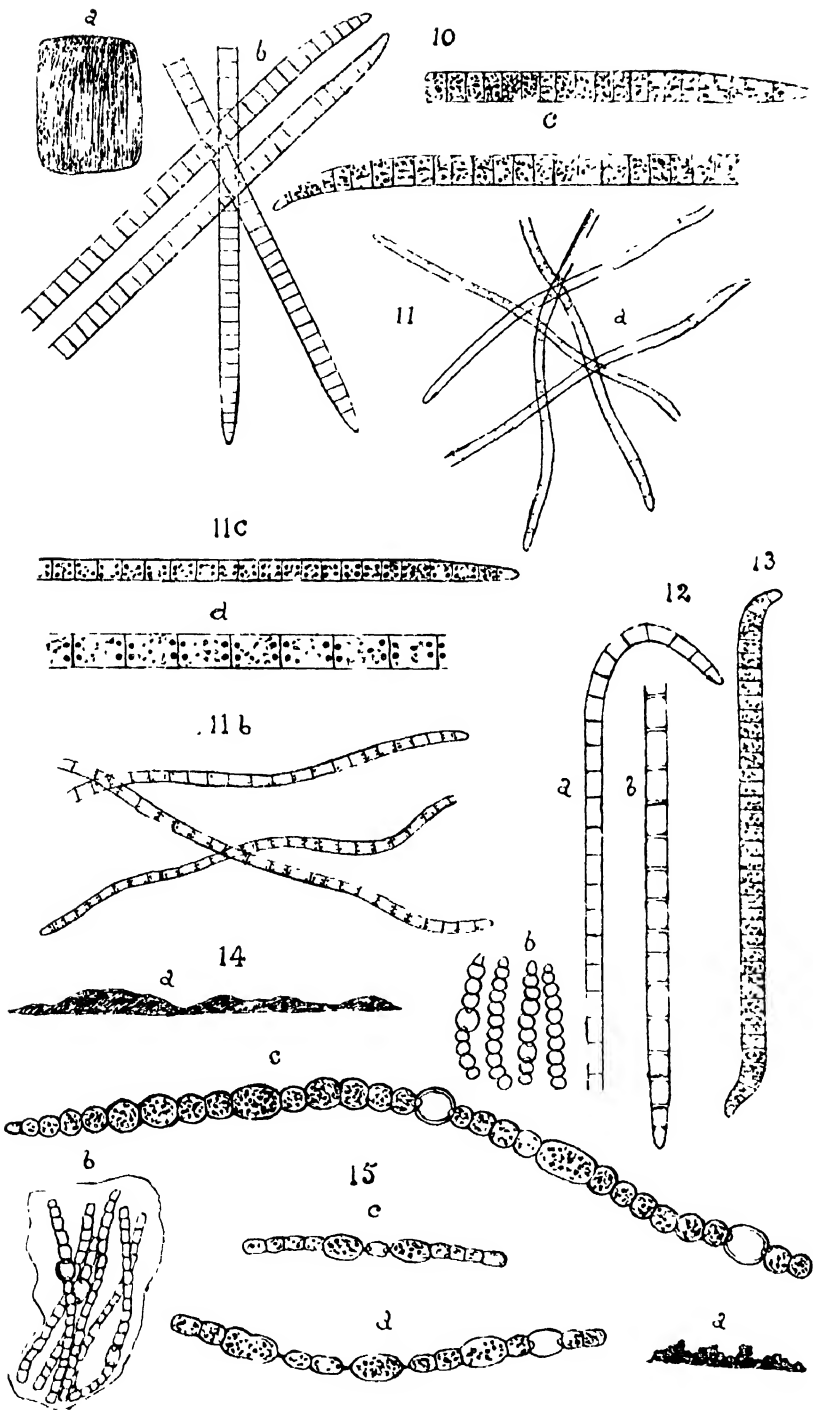
## PLATE I.

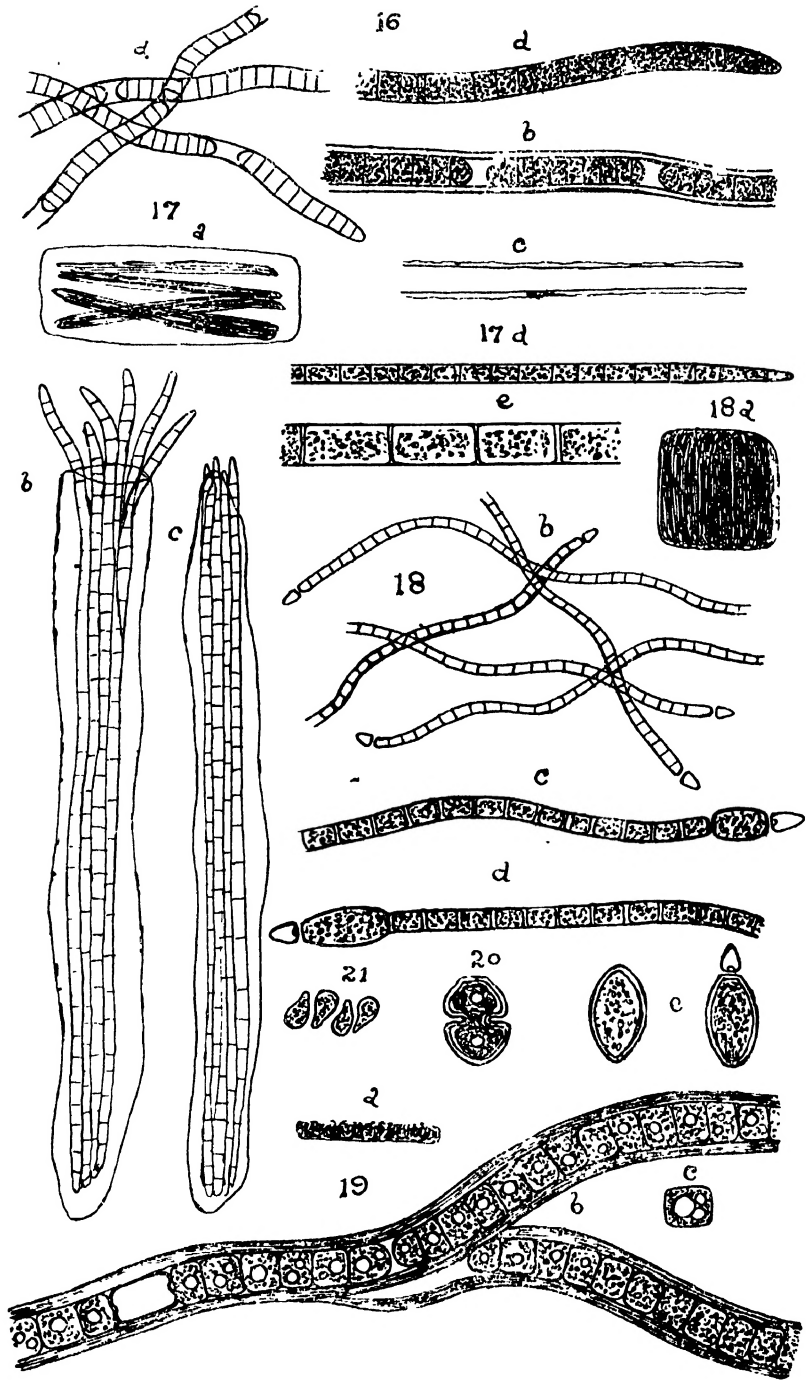
- Fig. 1. (*a-c*) *Chroococcus turgidus*,  $\times 500$ .  
Fig. 2. (*a-d*) *Chroococcus minutus*,  $\times 600$ .  
Fig. 3. (*a-b*) *Gloeocapsa quaternata*,  $\times 350$ .  
Fig. 4. *Aphanocapsa brunea* :  
    (*a*) plant mass,  
    (*b*) cells and their division,  $\times 350$ ,  
    (*c*) dried-up cells at high temperature,  $\times 500$ .  
Fig. 5. *Aphanocapsa Grevillei* :  
    (*a*) plant mass,  
    (*b*) cells and their division,  $\times 600$ .  
Fig. 6. *Oscillatoria princeps* :  
    (*a*) bunch of filaments,  $\times 350$ ,  
    (*b*) part of a filament showing the apex,  $\times 350$ .  
Fig. 7. *Oscillatoria tenuis* :  
    (*a*)  $\times 850$ ,  
    (*b*)  $\times 1000$ .  
Fig. 8. *Oscillatoria amphibia* :  
    (*a*) bunch of filaments,  $\times 1000$ ,  
    (*b*) a single filament showing the contents,  $\times 1500$ .  
Fig. 9. *Oscillatoria calcutrensis* :  
    (*a*) bunch of filaments,  $\times 1000$ ,  
    (*b*) filaments showing the contents,  $\times 1500$ ,  
    (*c*) part of the filament, highly magnified.

## EXPLANATION OF FIGURES.

## PLATE II.

- Fig. 10. *Oscillatoria animalis* :  
(a) plant mass,  
(b) filaments showing the partition walls,  $\times 750$ ,  
(c) filaments showing the contents,  $\times 1000$ .
- Fig. 11. *Oscillatoria quadripunctulata* :  
(a) bunch of filaments,  $\times 800$ ,  
(b) bunch of filaments with partition walls marked by two granules on either side,  $\times 1000$ ,  
(c) a filament showing the contents,  $\times 2000$ ,  
(d) part of a filament, highly magnified.
- Fig. 12. *Phormidium tenue* :  
(a) a filament showing the partition wall,  $\times 1000$ ,  
(b) a filament treated with formalin alcohol, 10%, and stained in haematoxylin,  $\times 1500$ .
- Fig. 13. *Oscillatoria acula*,  $\times 500$ .
- Fig. 14. *Nostoc Commune* :  
(a) plant mass,  
(b) bunch filaments,  $\times 500$ ,  
(c) part of a filament showing the contents and gonidia,  $\times 750$ .
- Fig. 15. *Nostoc sphaericum* :  
(a) plant mass,  
(b) bunch of filaments,  $\times 250$ ,  
(c) part of a filament showing gonidia on either side of the heterocyst,  $\times 500$ ,  
(d) part of a filament showing gonidia away from the heterocyst,  $\times 750$ .





## EXPLANATION OF FIGURES.

## PLATE III.

Fig. 16. *Lyngbya aeurugineo-coerulea* :

- (a) bunch of filaments,  $\times 500$ ,
- (b) part of a filament with the sheath,  $\times 650$ ,
- (c) part of the sheath of a filament without the trichome,  $\times 600$ ,
- (d) part of a filament showing the apex without the sheath,  $\times 650$ .

Fig. 17. *Microcoleus paludosus* :

- (a) plant mass,
- (b), (c) filaments enclosed in the sheath,  $\times 300$ ,
- (d) part of a filament showing the apex without the sheath,  $\times 500$ ,
- (e) part of a filament, highly magnified.

Fig. 18. *Cylindrospermum bengalense* :

- (a) plant mass,
- (b) bunch of filaments,  $\times 650$ ,
- (c), (d) part of filaments showing the contents and gonidia,  $\times 1000$ ,
- (e) two gonidia,  $\times 700$ .

Fig. 19. *Seytonema mirabilis* :

- (a) plant mass,
- (b) a filament,  $\times 450$ ,
- (c) a cell showing the vacuole,  $\times 450$ .

Fig. 20. *Cosmarium granatum*,  $\times 550$ .

Fig. 21. *Scenedesmus obtusus*,  $\times 500$ .

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